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CXLVI.—*Polymorphic Nitrobenzaldehydehydrazones.*

By FREDERICK DANIEL CHATTAWAY and ARTHUR JOHN WALKER.

MANY nitrobenzaldehydehydrazones exist in polymorphic modifications. *o*-Nitrobenzaldehyde-2-chloro-4-bromophenylhydrazone, *p*-nitrobenzaldehyde-2 : 4-dichlorophenylhydrazone, *p*-nitrobenzaldehyde-4-chloro-2-bromophenylhydrazone, and *p*-nitrobenzaldehyde-2-chloro-4-bromophenylhydrazone, which are characteristic examples, have been more fully investigated. Each of the first three exists in two well-defined forms, a yellow or orange labile form, which almost invariably separates when warm saturated solutions are allowed to cool, and a dark red, compact, stable form into which the labile is transformed if left in contact with a solvent. The fourth compound, *p*-nitrobenzaldehyde-2-chloro-4-bromophenylhydrazone, is trimorphic, the least stable, a yellow, hair-like form, transforming into orange needles and these into dark red, compact, rhombic crystals.

The solubilities in alcohol of the labile and stable forms when plotted gave in every case curves which are practically parallel. The range of temperature over which both determinations were possible is too limited to allow any trustworthy deductions to be drawn as to the position of a possible transition temperature.

In these hydrazones, the solubility ratios—labile : stable—are exceptionally large, indicating a much higher value for the energy of transformation than has hitherto been found in polymorphic organic compounds. In the following table these ratios at 15° are compared with the corresponding ratios of some polymorphic anilides and hydrazides previously examined (Chattaway and Lambert, J., 1915, **107**, 1766).

	Solubility ratio. Labile : Stable.	Energy of transformation (cals.) per mol. Calculated as $RT(\log s_1 - \log s_2)$.
p-Bromoacetanilide	1·08	44·0
2-4 : Dibromoacetanilide	1·19	99·5
Phthalylphenylhydrazide	1·013	7·2
Phthalylphenylmethylhydrazide	1·214	111·0
p-Nitrobenzaldehyde-2 : 4-dichlorophenylhydrazone	1·44	208·5
o-Nitrobenzaldehyde-2-chloro-4-bromophenylhydrazone	1·63	279·0

The four *p*-nitrobenzaldehyde-2 : 4-dihalogenophenylhydrazones crystallise either in the orthorhombic system, the monoclinic system, or a yellow, hair-like form of undetermined system, and a close relationship exists between the crystals of each class. Only in

the case of the 2-chloro-4-bromophenylhydrazone have all three types of crystal been realised in the same compound, but it is probable that each of the other members of the series is capable of existing in three similar and probably isotrimorphous forms.

EXPERIMENTAL.

When a hot saturated solution of *p*-nitrobenzaldehyde-2 : 4-dichlorophenylhydrazone, for example, is allowed to cool, pale orange needles of the labile form invariably separate and grow rapidly until the whole liquid is filled with a mass of fine interlacing crystals, which when dry may be kept for an indefinite period without any perceptible change. If, however, they are allowed to remain in the mother-liquor, tiny, glistening points of the stable red modification make their appearance and grow at the expense of the labile form, which slowly redissolves and disappears completely. Finally only a thin layer of compact red crystals remains on the bottom of the vessel. If the orange needles are just covered with alcohol and heated on a water-bath, they are converted into the red form in a few minutes.

The stable and labile forms of *o*-nitrobenzaldehyde-2-chloro-4-bromophenylhydrazone and of *p*-nitrobenzaldehyde-4-chloro-2-bromophenylhydrazone were prepared in a similar manner. Warm solutions of the trimorphic *p*-nitrobenzaldehyde-2-chloro-4-bromophenylhydrazone generally deposit the two labile forms together as a mixture of yellow, hair-like crystals and orange needles. Consequently the preparation of each of these forms in a pure state is somewhat difficult, and the least stable, hair-like form has only been obtained free from the orange needles by mechanical separation. The intermediate needle-like form alone is produced from *slowly* cooling, undisturbed solutions, seeded with a few well-chosen crystals of this variety.

The transformation of either of these labile forms into the stable red form is extremely slow at the ordinary temperature, and the latter is best prepared by heating a mixture of the other two, obtained as described above, with a little glacial acetic acid near its boiling point, when 5 or 10 minutes suffice to complete the change.

To obtain a rough estimate of the rates of transformations of the labile modifications in contact with different solvents, a hot saturated solution of each compound was chilled, and the suspension of fine needles of the labile form so produced seeded with a small quantity of the stable variety and left undisturbed at the ordinary temperature. The time taken for complete transformation was then noted. The following times were required:

		Alcohol.	Acetic acid.	Acetone.	Benzene.	Chloroform.	Chloroform at −20°.
p-Nitrobenzaldehyde-2 : 4-dichlorophenylhydrazone.		5 days	2½ days	30 hours	24—30 hours	16—20 hours	2 days
o-Nitrobenzaldehyde-2-chloro-4-bromophenylhydrazone.		2 days	24 hours	16—20 hours	7 hours	4—5 hours	1 day
p-Nitrobenzaldehyde-4-chloro-2-bromophenylhydrazone.		15—20 hours	20 hours	—	3—4 hours	3—4 hours	16—20 hours
p-Nitrobenzaldehyde-2-chloro-4-bromophenylhydrazone.	Hair-like form to orange needles.	7 days	2½ days	—	—	12 hours	—
	Orange needles to dark red form.	Very slow in all solvents at laboratory temperature, requiring several weeks for complete change.					

Since the ratio of the solubility of the labile form to that of the stable form at any temperature is constant and independent of the solvent employed, a greater solubility of both forms is accompanied by a greater *difference* between their solubilities and a greater supersaturation relative to the stable form when both forms are present. Transformation should therefore proceed more rapidly, other conditions being the same, in those solvents in which the substance is more soluble. This influence of the solvent upon the velocity of transformation is apparent from the results given in the above table, but since other factors incapable of control (for example, the size of the crystals and their relative numbers) play an important part in the changes, the rates of transformation observed correspond only roughly with the solubilities in the particular solvents.

Stability Relations of the Polymorphs.

In the presence of a solvent the change from one form to another was generally rapid and could easily be detected by the alteration in the colour and form of the crystals. Between — 20° and 118° chloroform, alcohol, and acetic acid were employed as solvents. At temperatures from 120° to the melting points—near 200°—the transformations were carried out in small sealed tubes, containing a mixture of the crystalline forms moistened with alcohol, immersed in an oil-bath at a constant temperature. Observations were made at intervals of 20° up to about 5° below the melting point, this being about the temperature at which the hydrazones liquefied under the solvent. The three dimorphic hydrazones are monotropic, transformation into the dark red form occurring in each case from — 20° to within a few degrees of the melting point of the particular compound.

The orange, needle-like form and the dark red, compact form of the trimorphic *p*-nitrobenzaldehyde-2-chloro-4-bromophenylhydrazone are enantiotropic. Below 150° the orange crystals pass into the dark red, whilst at 160° and higher temperatures up to the melting point, 195°, the reverse change occurs and the orange form appears to be the stable one. The change of volume accompanying the transition was so slight that the dilatometric method could not be employed; the transition temperature, however, was determined within comparatively narrow limits as follows. A mixture of the red and orange crystals of moderate size was moistened with alcohol and spread in a thin layer on one side of a sealed tube suspended in an oil-bath. A strong light was placed behind the tube, and the appearance of the separate crystals observed through a microscope whilst the temperature was raised by intervals of half a degree. Growing crystals showed sharp and clearly defined edges, whereas those which were dissolving had a cloudy, etched appearance, and their edges appeared smooth and rounded. At 153°, the dark red crystals were unmistakably growing, and at 155·5° definite indications of the slow growth of the orange form were perceptible. The transition temperature must therefore be between these limits, and lie in the neighbourhood of 154°.

The third, yellow, hair-like modification of this substance is labile with respect to each of the other two at all temperatures examined. Above the transition point of the orange-red form, it changes into the orange form. Below this temperature, it transforms first into the orange, and finally into the dark red, compact form.

As in the case of other polymorphic compounds of high melting point, the different forms of the same hydrazone appear to melt at the same temperature. The probability that in all such cases the labile form reverts to the stable one at or below its own melting point, which is therefore never observed, is supported by the following evidence. Molten *o*-nitrobenzaldehyde-2-chloro-4-bromophenylhydrazone, in a thin film between a microscope slide and cover-glass, was allowed to cool. Generally patches of both crystalline forms were produced, which were readily distinguishable in polarised light, only one form being pleochroic. Several slides prepared in this manner were maintained at 180° for 1 or 2 hours; in every case complete transformation into the stable, pleochroic form (m. p. 191·5°) had taken place.

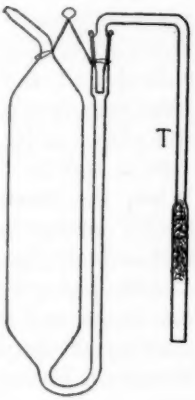
In the case of *p*-nitrobenzaldehyde-2:4-dichlorophenylhydrazone, both forms could be kept in contact for 3 to 4 hours between 195° and 200° without any perceptible change. The latter temperature is so near the melting point, 202°, that there can be very little

difference between the melting points of the two forms. This suggests the possibility of a transition point near the melting point, and the fact that the two corresponding forms of *p*-nitrobenzaldehyde-2-chloro-4-bromophenylhydrazone are enantiotropic and have a transition point only some 40° below the melting point lends some support to this view.

Solubilities in Ethyl Alcohol.

The solubilities of both forms of *p*-nitrobenzaldehyde-2 : 4-dichlorophenylhydrazone and of *o*-nitrobenzaldehyde-2-chloro-4-bromophenylhydrazone in alcohol were determined between 0° and 35° or 40°. The instability of the labile form of *p*-nitrobenzaldehyde-4-chloro-2-bromophenylhydrazone rendered satisfactory determinations of its solubility impossible even at 0°.

FIG. 1.



Finely divided crystals of the hydrazones were shaken with the solvent in a thermostat (control $\pm 0{\cdot}02°$) for a number of hours previously ascertained to be more than sufficient to ensure saturation. A standard thermometer of range -10—$50°$, graduated in tenths of a degree and readable to $0{\cdot}01°$ with the aid of a lens, was used.

The purest absolute alcohol obtainable was dehydrated over quicklime, twice fractionated from calcium turnings, and freed from a trace of ammonia (produced by the decomposition of small quantities of calcium nitride present in the metal) by refractionation from a small quantity of phosphorus pentoxide. Trial experiments showed that at the ordinary temperature 1—2 hours' shaking in the thermostat ensured saturation with the powdered crystals of the stable forms, whilst the labile modifications required from $\frac{1}{2}$ to $\frac{3}{4}$ hour. In actual determinations, the stable forms were shaken for 4 to 6 hours and the labile forms for 1—2 hours.

The saturated solutions were removed in a pipette of the type shown in Fig. 1. The detachable tube, *T*, containing a plug of cotton wool through which the solution filtered before it entered the pipette, was removed before weighing. Contact of the solution with the ground joint was prevented by means of the short extension of the tube into the pipette.

As in the case of the polymorphic anilides (Chattaway and Lambert, J., 1915, **107**, 1766), the amount of hydrazone dissolved was estimated by evaporating the solvent from a weighed quantity

of solution, and weighing the solid residue. Preliminary experiments showed that the hydrazones were unaffected by this treatment. No appreciable change of weight could be detected after three evaporations, and no volatilisation or oxidation of the solid could therefore have occurred in the process.

The glass apparatus was cleaned with concentrated sulphuric acid, distilled water, and alcohol in succession. The corks were boiled in the solvent just before use.

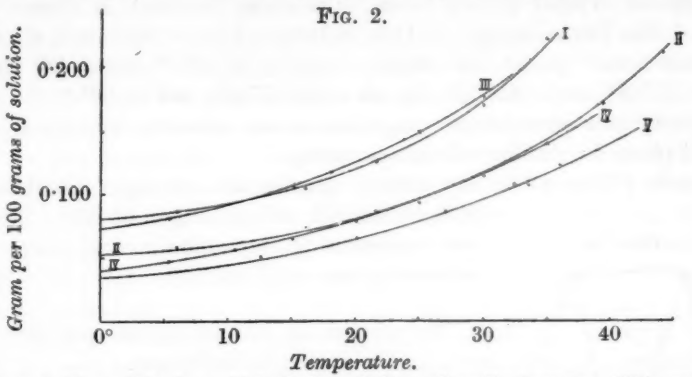
A solution of the hydrazone almost saturated at its boiling point was filtered into an equal volume of the hot solvent, and the resulting solution again filtered into the solubility bottle, which contained a further small quantity of the hot solvent. The solution in the bottle was boiled gently for a few minutes to ensure the complete disappearance of crystalline nuclei, and then more vigorously until the condensing vapour had thoroughly washed down the sides and neck of the bottle. The bottle was immediately corked and the contents were chilled, when the orange, labile form usually separated as a pulp of fine needles. Before the bottle was placed in the bath to be shaken, the neck and cork were covered with a tightly fitting rubber cap to prevent the access of water. When the above precautions were observed, it was possible to obtain suspensions of the labile forms of *p*-nitrobenzaldehyde-2 : 4-dichlorophenylhydrazone and of *o*-nitrobenzaldehyde-2-chloro-4-bromophenylhydrazone which could be used for solubility determinations, and showed no sign of transformation after 4 or 5 hours' shaking at temperatures below 20°. Between 25° and 35° transformation invariably began in less than 4 hours; although saturation at these temperatures could be attained within this period, it was difficult to determine the minimum time required. The state of saturation was approached from each side—supersaturation and unsaturation—and the agreement of the two sets of values obtained showed that saturation had been reached in all the experiments recorded.

The presence or absence of the glistening, red, stable form in the pulpy suspension of the labile modification was never in doubt; with the aid of a lens a minute quantity of the former, if present, could easily be detected.

A labile suspension could not be used for more than one determination, for when the bottle was opened for the removal of some of the solution for analysis, air infected with the stable form entered, and the suspension, if shaken again, soon showed signs of transformation. The results of the solubility determinations are shown graphically in Fig. 2. The solubility data are recorded below with the descriptions of the crystalline forms of the hydrazones.

The crystals of the stable forms were in every case well adapted for measurement. For this purpose, they were grown from warm

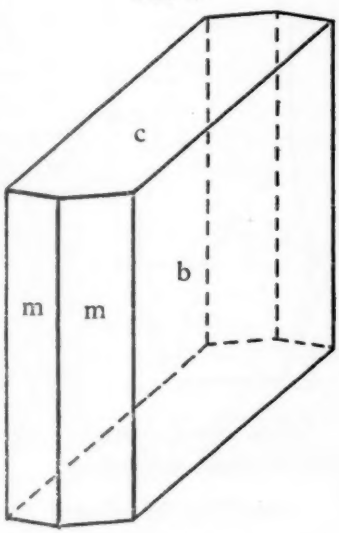
FIG. 2.



I *and* II p-*Nitrobenzaldehyde*-2 : 4-*dichlorophenylhydrazone.* III *and* IV o-*Nitrobenzaldehyde*-2-*chloro*-4-*bromophenylhydrazone.* V p-*Nitrobenzaldehyde*-4-*chloro*-2-*bromophenylhydrazone.*

chloroform solutions which were allowed to cool very slowly in a large water-jacketed vessel. The labile crystals were never sufficiently developed for measurement, but as far as it was possible a microscopic examination of these was made.

FIG. 3.



o-*Nitrobenzaldehyde*-2-*chloro*-4-*bromophenylhydrazone.*—*Stable Form.*—Thin red tablets. System monoclinic ($a : b = 0{\cdot}4006 : 1$. $\beta = 99° 53'$). A typical crystal is shown in Fig. 3, the forms being $b\{010\}$, $c\{001\}$, and $m\{110\}$. Measurements (mean of three): $bm = 68° 28'$, $bc = 90° 0'$, $cm = 80° 49'$. There is no cleavage. Optically the crystals are strongly pleochroic. Extinction on $b = 36°$ with edge *mm*.

Labile Form.—Microscopic, six-sided needles exhibiting straight extinction and strong pleochroism.

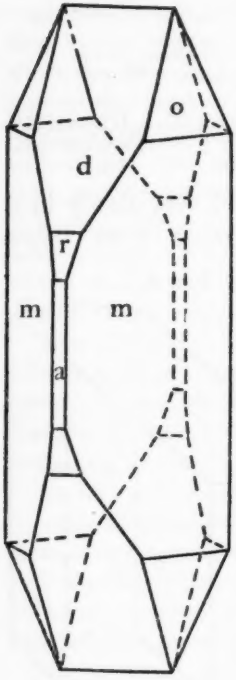
Solubilities in Alcohol (gram per 100 grams of solution).

Temp.	Stable form.	Labile form.	Temp.	Stable form.	Labile form.	Temp.	Stable form.	Labile form.
0·05°	0·039	0·073	15·00°	0·065	0·106	25·00°	0·093	0·150
5·25	0·047	0·082	18·00	—	0·118	30·00	0·116	0·179
10·50	0·056	0·093	20·00	0·079	—	37·95	0·159	—

p-*Nitrobenzaldehyde*-2 : 4-*dichlorophenylhydrazone.*—*Stable Form.*—Dark red crystals. System orthorhombic ($a:b:c = 1{\cdot}645:1:2{\cdot}081$) A typical crystal grown from chloroform solution is shown in Fig. 4, the forms being: $m\{110\}$, $a\{100\}$, $o\{111\}$, $d\{101\}$, and $r\{201\}$. Measurement (mean of three): $am = 58°\,42'$,* $ad = 38°\,19'$,* $ar = 21°\,20'$, $ao = 61°\,13'$ (3), $do = 52°\,7'$ (6), $md = 66°\,3'$ (− 6). Optically not pleochroic; negative acute bisectrix normal to a. Axial plane b; double refraction strong.

Labile Form.—The flat orange needles are strongly pleochroic, and extinguish at an angle of 32°. They are presumably monoclinic and have a terminal plane angle of 60°.

FIG. 4.



Solubilities in Alcohol (gram per 100 grams of solution).

Temp.	Stable form.	Labile form.	Temp.	Stable form.	Labile form.
0·05°	0·052	0·079	29·85	0·115	0·173
5·85	0·057	0·086	34·80°	0·142	0·225
11·90	0·064	0·097	38·00	—	—
16·00°	0·075	0·105	39·35	0·173	—
21·50	0·087	0·126	44·15	0·214	—

p-*Nitrobenzaldehyde*-4-*chloro*-2-*bromophenylhydrazone.*—*Stable Form.*—The dark red, orthorhombic crystals are isomorphous with those of the corresponding dichloro-compound, and exhibit the same forms, the only differences being a slight elongation along the b axis and the presence of the form $c\{001\}$. Axial ratios $a:b:c = 1{\cdot}691:1:2{\cdot}148$. Measurements (mean of three): $am = 59°\,24'$,* $cd = 51°\,39'$,* $cr = 68°\,20'$ (5), $ca = 90°\,0'$, $ao = 61°\,51'$ (− 5), $do = 53°\,1'$ (− 2), $md = 61°\,44'$ (4). The optical properties are in every way similar to those of the dichloro-compound.

Labile Form.—Bright yellow, hair-like needles, non-pleochroic, with straight extinction.

Solubility in Alcohol (gram per 100 grams of solution).

Temp.	0·05°	12·50°	20·00°	26·90°	33·50°	40·05°
Stable form	0·034	0·052	0·066	0·087	0·109	0·141

p-*Nitrobenzaldehyde*-2-*chloro*-4-*bromophenylhydrazone.*—*Stable Form.*—Stable below 154°. The orthorhombic, red crystals are isomorphous with the stable modifications of the preceding derivatives.

The same forms were observed, and in addition *p*{112}. $a : b : c = 1{\cdot}634 : 1 : 2{\cdot}076$. Measurements (mean of three): $am = 58° 32'$,* $ad = 38° 12'$,* $ar = 21° 41'$ (− 12), $ca = 90° 1'$ (− 1), $cm = 89° 59'$ (1), $co = 68° 1'$ (− 19), $cp = 50° 44'$ (− 5), $od = 52° 12'$ (− 6). Optically similar to the foregoing compounds.

Labile Forms. (a) *Monoclinic Form.*—Stable above 154°. The orange needles show a close resemblance to the monoclinic crystals of the corresponding 2 : 4-dichloro- and 2 : 4-dibromo-compounds. They are pleochroic in the same directions, having a 32° extinction and a terminal angle of 60°. (b) *Hair-like Form.*—The fine, yellow, non-pleochroic needles show straight extinction and correspond with the labile crystals of *p*-nitrobenzaldehyde-4-chloro-2-bromophenylhydrazone.

p-*Nitrobenzaldehyde*-2 : 4-*dibromophenylhydrazone.*—Orange, pleochroic needles; similar to the monoclinic forms of the corresponding 2 : 4-dichloro- and 2-chloro-4-bromo-compounds. Extinction 30°. Terminal angle 59°. The only form observed.

THE QUEEN'S COLLEGE, OXFORD. [*Received, February 21st,* 1924.]

CXLVII.—*A New Method for the Preparation of Thiocarbohydrazide: Mono- and Di-thio*-p-*urazine.*

By PRAPHULLA CHANDRA GUHA and SATISH CHANDRA DE.

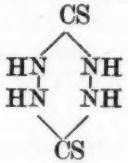
THIOCARBOHYDRAZIDE (Curtius and Heidenreich, *J. pr. Chem.*, 1895, [ii], **52**, 586; Stollé and Bowles, *Ber.*, 1908, **41**, 1099) has been prepared by the condensation of hydrazine hydrate (2 mols.) with diethyl xanthate (1 mol.):

$$OEt{\cdot}CS{\cdot}SEt + 2N_2H_4 = SC(NH{\cdot}NH_2)_2 + EtOH + EtSH.$$

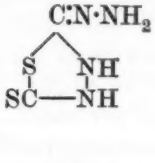
Thiocarbohydrazide and carbohydrazide react with thiocarbimides, yielding bisthiocarbamyl derivatives (X = S or O):

$$XC(NH{\cdot}NH_2)_2 + 2RCNS = XC(NH{\cdot}NH{\cdot}CS{\cdot}NHR)_2.$$

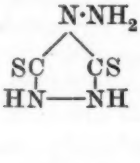
Potassium ethyl xanthate reacts with thiocarbohydrazide, giving a compound, $C_2H_4N_4S_2$, m. p. 202—203°, which has acid properties and forms a *disilver* salt and a *dibenzyl* ether but no benzylidene derivative. These properties harmonise with the constitution of *dithio*-p-*urazine* (I) and exclude the alternative structures (II and III).



(I.)



(II.)



(III.)

Purgotti and Vigano's feebly basic "dithio-*p*-urazine," m. p. 198—199°, obtained by the action of hydrazine hydrate on hydrazinedicarbonthioamide (*Gazzetta*, 1901, **31**, ii, 563), forms a monosilver salt and a benzylidene derivative and is probably the thiodiazole (II) (compare, however, Stollé, *J. pr. Chem.*, 1907, [ii], **75**, 423; Arndt and Bielich, *Ber.*, 1923, **56**, [*B*], 809).

Monothio-p-*urazine* (IV) has been prepared by the action of (i) carbamide on thiocarbohydrazide and (ii) potassium ethyl xanthate on carbohydrazide:

$$OC\langle{}^{NH\cdot NH_2}_{NH\cdot NH_2} \xrightarrow{OEt\cdot CS\cdot SK} OC\langle{}^{NH\cdot NH}_{NH\cdot NH}\rangle CS \xleftarrow{CO(NH_2)_2} {}^{NH_2\cdot NH}_{NH_2\cdot NH}\rangle CS$$

(IV.)

The action of carbamide on carbohydrazide yields *p*-urazine.

Experimental.

Thiocarbohydrazide.—To an alcoholic solution of 12 grams of diethyl xanthate, heated under reflux, an alcoholic solution of 8 grams of hydrazine hydrate was added during half an hour. Heating was continued for thirty minutes, ethyl mercaptan being evolved, and the white solid was then crystallised from boiling water (yield 70 per cent.). It was soluble in caustic alkalis, mineral acids, and ammonia, but insoluble in most of the organic solvents, formed insoluble barium and calcium salts, and reduced rapidly a cold ammoniacal solution of silver nitrate; on oxidation with iodine or ferric chloride, nitrogen was evolved. It decomposed at 170° with evolution of hydrogen sulphide and ammonia and the residue melted at 203° (Found: N = 53·01; S = 30·32. Calc., N = 52·83; S = 30·19 per cent.).

The *diacetyl* derivative was prepared by heating 3 grams of thiocarbohydrazide with an excess of acetic anhydride for 15 minutes. Nothing separating on dilution with water, the solution was distilled at 120° under reduced pressure, and the residual syrup dried at 110° and then over solid caustic potash in a vacuum. The extremely hygroscopic product was soluble in all organic solvents and melted at 180—181° (Found: N = 29·46; S = 16·95. $C_5H_{10}O_2N_4S$ requires N = 29·47; S = 16·84 per cent.).

Dimethylenethiocarbohydrazide separated as a white mass when 1·8 grams of thiocarbohydrazide were heated with an excess of 40 per cent. formaldehyde. It was insoluble in most of the ordinary organic solvents; crystallised from alcohol, it melted at 204—205° (decomp.) (Found: N = 43·29; S = 24·69. $C_3H_6N_4S$ requires N = 43·08; S = 24·62 per cent.).

Carbohydrazide- and Thiocarbohydrazide-dicarbonthiophenyl (*and p-tolyl*)-*amides*, $XC(NH\cdot NH\cdot CS\cdot NHR)_2$ (X = O or S; R = Ph or

p-C_7H_7).—These compounds were prepared by heating an alcoholic solution of the arylthiocarbimide (3 grams) with an aqueous solution of carbohydrazide (1 gram) or with a hydrochloric acid solution of thiocarbohydrazide (1 gram), and all but one were crystallised from a large quantity of alcohol. The odour of a carbylamine was perceptible when they were decomposed by iodine, ferric chloride, or boiling, concentrated aqueous potassium hydroxide. The compound for which X = S and R = Ph melts at 199° (Found: N = 22·56; S = 25·71. $C_{15}H_{16}N_6S_3$ requires N = 22·34; S = 25·53 per cent.). X = S; R = *p*-C_7H_7: This substance, purified by precipitation from alkaline solution with dilute hydrochloric acid, melts at 201° (Found: N = 20·82; S = 23·62. $C_{17}H_{20}N_6S_3$ requires N = 20·79; S = 23·76 per cent.). X = O; R = Ph: The compound melts at 208—209° (Found: N = 23·23. $C_{15}H_{16}ON_6S_2$ requires N = 23·33 per cent.). X = O; R = *p*-C_7H_7: The substance melts at 215—216° (Found: N = 21·77. $C_{17}H_{20}ON_6S_2$ requires N = 21·65 per cent.).

Dithio-p-*urazine*.—A mixture of 2 grams of thiocarbohydrazide, 3 grams of potassium ethyl xanthate, and 20 c.c. of alcohol was heated in a sealed tube at 100° for 5—6 hours with occasional shaking. After cooling, the liquid was decanted, the solid product dissolved in water, and the combined solutions, filtered from unchanged thiocarbohydrazide, were acidified with concentrated hydrochloric acid. The solid that separated was insoluble in all organic solvents, but moderately soluble in hot water, and was crystallised from a hot aqueous solution by addition of a few drops of hydrochloric acid. It melted at 202—203° (Found: N = 37·68; S = 43·34. $C_2H_4N_4S_2$ requires N = 37·84; S = 43·24 per cent.).

The *disulphide*, m. p. 218° (decomp.), obtained by adding a solution of iodine to an aqueous solution of the preceding compound, was insoluble in all organic solvents (Found: N = 38·76; S = 43·96. $C_2H_2N_4S_2$ requires N = 38·36; S = 43·83 per cent.).

The *dibenzyl* ether was prepared by heating dithio-*p*-urazine (1 mol.) with alcoholic potassium hydroxide (2 mols.) and benzyl chloride (2 mols.) for 10 minutes, and separated from the filtered, cooled solution as a white, crystalline mass, which was triturated with water and crystallised from alcohol; m. p. 142° (Found: S = 19·38. $C_{16}H_{16}N_4S_2$ requires S = 19·51 per cent.).

The dull yellow *silver* salt was precipitated on addition of silver nitrate to a hot solution of dithio-*p*-urazine in dilute nitric acid (Found: Ag = 59·74; S = 17·80. $C_2H_2N_4S_2Ag_2$ requires Ag = 59·66; S = 17·68 per cent.).

Monothio-p-*urazine*.—A mixture of 4 grams of thiocarbohydrazide and 8 grams of carbamide was heated at 130° for 5—6 hours,

when the evolution of ammonia ceased; after extraction with water, the residue, which was insoluble in the ordinary organic solvents, was dissolved in caustic soda solution; the solid precipitated by dilute hydrochloric acid melted and decomposed at 238° (Found: N = 42·66; S = 24·11. $C_2H_4ON_4S$ requires N = 42·42; S = 24·24 per cent.). The same compound was obtained by heating in a sealed tube at 100° 3 grams of carbohydrazide and 4·5 grams of potassium ethyl xanthate in alcoholic solution.

p-*Urazine*.—Three grams of carbohydrazide were heated with 8 grams of carbamide at 120° for 4—5 hours, when the evolution of ammonia ceased. The solid, washed with water and crystallised from the hot solvent, melted at 264—265° (Found : N = 48·46. Calc., N = 48·28 per cent.).

Further work in this direction is in progress.

Our thanks are due to Sir P. C. Rây, Dr. J. C. Ghosh, and Mr. S. N. Bose for the interest they have taken in the work.

THE UNIVERSITY, DACCA,
BENGAL, INDIA. [*Received, December 10th*, 1923.]

CXLVIII.—*Rate of Photochemical Change in Solids.*

By EDMUND JOHN BOWEN, HAROLD HARTLEY, WILLIAM DONALD SCOTT, and HAROLD GARFIT WATTS.

NUMEROUS examples are known of organic compounds which undergo photochemical transformation in the solid state, but the mechanism of the processes involved is at present obscure. It is therefore of interest to examine whether a molecule undergoes transformation when a quantum of photochemical energy is absorbed by it in the crystal lattice, in accordance with Einstein's law of the photochemical equivalence. Other possible alternatives are either that a proportion of the absorbed quanta is degraded into thermal energy, or that extensive secondary reactions occur resulting in the formation of a large number of molecules of product for each absorbed quantum.

The first reaction studied was the isomeric change of *o*-nitrobenzaldehyde into *o*-nitrosobenzoic acid, occurring in violet light. When the amount of change is less than about 2·5 per cent. the product remains in solid solution in the aldehyde (Lobry de Bruyn, *Rec. trav. chim.*, 1903, **22**, 298). In these experiments the amount of change was kept below this limit to avoid separation of the acid in white crystals impeding the absorption of light by the aldehyde. The photochemical reaction is a homogeneous one, occurring inside

the body of the crystals. Even within the solid-solution range, the light absorption is altered by the formation of the acid, which is green in the unimolecular state, and the amount of change was always kept low on this account.

A 1000 c.p. "Pointolite" lamp and an automatic carbon arc lamp were used as light sources, the light passing through a condensing lens and filters of solutions of copper sulphate and of crystal-violet. The energy in the radiation was measured with the air-thermometer previously described (Bowen, J., 1923, **123**, 2328). A weighed amount of the pure substance (m. p. 43°) was melted or spread in a thin layer on a watch-glass, covered with another glass, and exposed to the light for a known time. The amount of *o*-nitrosobenzoic acid formed was estimated by dissolving the material in 10 c.c. of benzene and extracting with 100 c.c. of conductivity water. The acid passed almost entirely into the water, and its concentration was found by measuring the electrical conductivity and comparing it with the measurements made with solutions of the acid of known concentration.

The amount of energy absorbed could not be measured accurately, because of the light lost by scattering owing to the irregular orientation of the crystals. The results are calculated on the assumption that all the light is absorbed, and the ratios of quanta/molecules must be diminished by the fraction of the energy lost, which was estimated roughly by comparison with a white substance as being less than 50 per cent.

Spectral range of filter. Å.	Time of exposure. Mins.	No. of quanta per sec. in radiation calc. at mean wave-length. $\times 10^{-15}$.	No. of mols. of *o*-nitrosobenzoic acid formed per sec. $\times 10^{-15}$.	Ratio $\frac{\text{Quanta}}{\text{Molecules}}$.
4000—4300	10	4·85	2·2	2·2
,,	15	4·85	2·26	2·1
3900—4400	,,	8·0	3·87	2·07
,,	12	,,	3·93	2·04
,,	8	,,	3·06	2·62
,,	5	,,	3·09	2·59
3950—4350	11	6·1	2·88	2·12
,,	3	6·1	2·22	2·75
,,	5	19·5	13·68	1·43
,,	6	,,	13·20	1·48
,,	7	,,	13·32	1·46

The greater apparent light efficiency in the last three experiments is to be attributed to the greater accuracy of the energy measurements with larger light intensities. The measurements of the feebler intensities are much more seriously affected by errors, which could not be eliminated, due to the warming of the air by the lamp. The results, however, are quite adequate to establish

the simplicity of the process of this photochemical change. When allowance has been made for energy not absorbed and for experimental errors, it appears that for each quantum of absorbed radiation very nearly one molecule of product is formed.

The photochemical change of cinnamylidenemalonic acid was also studied. This bright yellow substance is transformed by light into a colourless acid which is probably a dimeride, diphenyltetramethylenediethenyldicarboxylic acid (Riiber, *Ber.*, 1902, **35**, 2411). If the change is not carried too far the product remains in solid solution in the crystals. The colourless substance is more soluble in water than the yellow, and the amount of photochemical change was determined by allowing the substance after exposure to come into equilibrium at 18° with a known volume of conductivity water so that the yellow acid formed a saturated solution while the other was completely dissolved. The electrical conductivities of the solutions were then compared with those of mixtures containing known amounts of the colourless acid.

Spectral range of filter 4000—4550 Å.

Time of exposure. Mins.	No. of quanta per sec. in radiation calc. at mean wave-length. $\times 10^{-16}$.	No. of mols. of colourless acid formed per sec. $\times 10^{-16}$.	Ratio $\frac{\text{Quanta.}}{\text{Molecules}}$.
6	13·5	11·1	1·22
12	,,	8·2	1·65
4	8·5	8·35	1·02
5	,,	4·6	1·85
6	,,	9·7	0·88
7·5	,,	7·1	1·20
8	,,	8·33	1·02

It appears from these measurements that in the two reactions studied involving photochemical changes in the solid state one molecule is transformed for each quantum absorbed, within the limits of experimental error. These results throw some light on the mechanism of the change. The absorption of light by a substance is attended by the passage of a particular electron from one orbit to another of greater energy. In the common case of a substance not photochemically sensitive, the electron returns to its normal orbit after the lapse of a certain time, and in solids the energy usually appears as kinetic energy of the system. The average life of the electron in the higher quantum orbit is probably determined by the atomic vibration period within the molecule, which is of the order of 10^{-12} second. In these photochemical reactions investigated, every absorbed quantum seems effective in bringing about the change. This must mean that the probability of the electron losing its energy by deactivation before the change has occurred is small; that is, that the time of the primary reaction

is small compared with the atomic frequency, and therefore with the probable time of rearrangement of the atoms in the molecule. Possibly the primary change after the passage of the electron to the higher quantum orbit is the transfer of the electron from one atom to another, followed by secondary changes, namely the passage of the oxygen atom in the case of *o*-nitrobenzaldehyde from the nitro-group to the aldehydo-group, and by dimerisation in the case of cinnamylidenemalonic acid.

The experiment was made of comparing the action of plane-polarised light with that of ordinary light of nearly the same intensity. It was found with the crystals distributed at random that the same yield was obtained in both cases.

$$\text{Ratio of rates of change } \frac{\text{Ordinary light}}{\text{Plane-polarised light}} = 1{\cdot}33;\ 1{\cdot}24.$$

$$\text{Ratio of intensities } \frac{\text{Ordinary light}}{\text{Plane-polarised light}} = 1{\cdot}35.$$

By exposing thin crystals of these two substances under the microscope to polarised light, Padoa (*Atti R. Accad. Lincei*, **1919**, [v], **28**, ii, 372) found that the time for breaking up of the crystal owing to strain set up by solid-solution formation varied with the orientation. The crystals of these substances are doubly refracting, and two explanations are possible; either that the ordinary ray alone produces photochemical change, and that the perpendicular displacements of the extraordinary ray are ineffective; or that the absorption coefficient of the one ray is greater than that of the other (compare tourmaline) but that both are photochemically effective.

The second possibility is more likely, as it admits of a simple interpretation in terms of the wave theory and of the quantum theory. It is also in accordance with the experimental results. The first possibility would require, with a chaotic orientation of the crystals, that two absorbed quanta should correspond to one transformed molecule; whilst, in the case of the second, for each molecule a number of quanta between one and two should be absorbed, depending on the relative absorptions of the two rays. In accordance with this, the strongly coloured cinnamylidenemalonic acid gave numbers near unity, while the paler yellow *o*-nitrobenzaldehyde, which probably did not absorb the whole of the light even within the close spectral range employed, gave distinctly higher results.

BALLIOL AND UNIVERSITY COLLEGES,
OXFORD.

[*Received, March 18th*, 1924.

CXLIX.—*Investigations on the Supposed Existence of Copper Carbonyl.*

By Emile Mond and Christian Heberlein.

Bertrand (*Compt. rend.*, 1923, **177**, 997) tried to explain the metallisation of insects, observed by Zelinski in the course of the organic chemical analysis of bees (*ibid.*, p. 1041), by the formation of a copper carbonyl.

We repeated Bertrand's experiments and made the following observations:

(1) Finely divided copper oxide, heated in air, begins to cake and to adhere to the walls of the glass tube at 400°; at 600° (dark red heat), it forms a solid lump. On cooling in air, the cake disintegrates after several hours. Even at low temperatures, therefore, copper oxide has a great tendency to sinter and adhere to any surface.

(2) The reduction of copper oxide by hydrogen or carbon monoxide is an exothermic reaction. The heat given off is so great that the temperature of the reducing copper oxide is much higher than that of the surrounding glass tube. Even with a slow current of hydrogen, the glass tube being kept at 600°, the reaction zone glows brightly. The formation of metallic carbonyls also is an exothermic reaction and would assist in increasing the temperature. From these theoretical considerations, it appears unlikely that a copper carbonyl is formed at a red heat and is again decomposed at practically the same or even lower temperature.

(3) When copper oxide is reduced at 600° (dark red heat) with carbon dioxide containing carbon monoxide as prepared by Bertrand, or with pure hydrogen (made electrolytically or from zinc and sulphuric acid), the glass wall of the tube is covered with a brilliant purple-red mirror, which adheres firmly to the glass. The mirror is insoluble in concentrated nitric acid. The copper is therefore not present in the metallic state, but has entered into combination with the glass. (Soft and hard glass both form the red compound.) The red mirror is of a more purple colour than ordinary fine metallic copper. The higher the temperature during the reduction the more of the red compound is produced. At 500° only a faint mirror is formed.

(4) The reduced metallic copper shows a greater tendency than copper oxide to sinter at low temperatures; even at 400° it lumps together.

(5) Metallic copper heated in hydrogen or carbon monoxide at 600° forms no mirror.

(6) The formation of copper carbonyl can take place only at the moment the copper oxide is reduced.

If overheating is avoided as much as possible and the gas quickly transported to another, hotter, tube, any copper carbonyl formed should be decomposed on the second tube. A thin glass tube, filled with copper oxide and open at both ends, was inserted half-way into a wider tube. The latter was heated in an iron pipe in a combustion furnace at 550°. The temperature of the inner tube was 500°. When a current of carbon dioxide containing carbon monoxide was passed through the apparatus, no trace of a mirror formed on the second tube.

(7) As far as Bertrand's experiments and ours go, we can find no proof of the formation of copper carbonyl. We believe the metallisation can be explained by the adhesion and sintering of the copper oxide. The additional heat created by the reduction would help to increase these properties.

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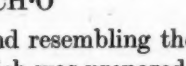
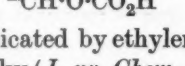
76, PETTY FRANCE, S.W. 1. [*Received, March 22nd*, 1924.]

CL.—*Sugar Carbonates and their Derivatives. Part I.*

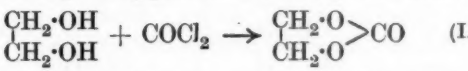
By CHARLES FREDERICK ALLPRESS and WALTER NORMAN HAWORTH.

A REVIEW of the nature and general behaviour of the sugars has led us to inquire into the prospect of preparing sugar carbonates and to consider the possibility of the natural occurrence of such compounds. These substances should conform to two types represented by the normal and acid carbonates :

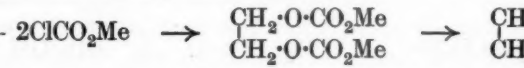

(A)


(B)

A compound resembling the former is indicated by ethylene carbonate (I), which was prepared by Nemirowsky (*J. pr. Chem.*, 1883, [ii], 28, 439) from ethylene glycol and carbonyl chloride :


(I.)

We also have prepared it by condensing the sodium derivative of ethylene glycol with methyl chloroformate,



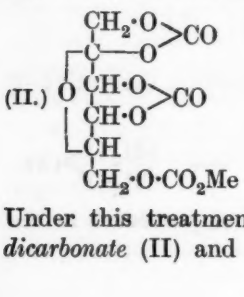
and this reaction suggested a possible method of procedure in the sugar group.

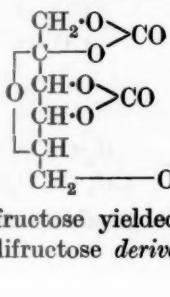
Ethylene carbonate may be regarded as the oxygen analogue of glycol acetone, $\begin{matrix}CH_2\cdot O\\ CH_2\cdot O\end{matrix}>CMe_2$, and indeed, we have discovered that the acetone series of sugar derivatives is comparable in many respects. The normal carbonates of the sugars which are described in this communication resemble the acetone derivatives in their tendency to crystallisation, and their ease of hydrolysis with dilute acids, but the carbonates are characterised by the great readiness with which they may be hydrolysed to the free sugars with dilute alkali or baryta on gentle warming.

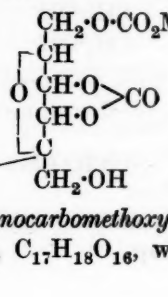
These features endow the new series of sugar derivatives with special interest owing to the possibility of their utilisation in synthetic work leading to the disaccharides. Several of the sugar carbonates of the type B possess one exposed hydroxyl group through which condensation with a similar sugar residue may occur. Since the carbonic acid substituent is easily eliminated by mild reagents which should not disturb the newly-formed biose linking, these sugar derivatives may serve to circumvent some of the disadvantages of the methylated sugars in that the methyl group in the latter may only be eliminated by drastic hydrolytic agents such as hydriodic acid, which simultaneously effects the cleavage of a disaccharide.

Two general methods of preparing the sugar carbonates have been adopted and these are analogous to the conditions applied by E. Fischer and his co-workers to the case of phenolic acids. In the first method, an aqueous solution of a hexose was cooled below 0° and mixed with the appropriate quantity of methyl or ethyl chloroformate. To this there was gradually added dilute alkali, with vigorous stirring, and during this operation the product usually separated from the aqueous medium as a viscid liquid which afterwards, in the cases of several of the hexoses, crystallised from organic solvents. The structural formulæ of these products must for the present be tentative, since even the acetone derivatives of the hexoses, which were prepared by Fischer so long ago as 1895 (*Ber.*, **28**, 1145), are still indicated by provisional constitutional formulæ.

(II.)



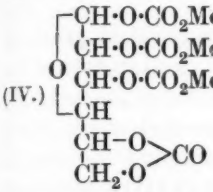




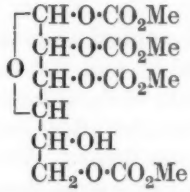
(III.)

Under this treatment, fructose yielded *monocarbomethoxy fructose dicarbonate* (II) and a difructose *derivative*, $C_{17}H_{18}O_{16}$, which for

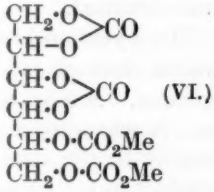
the present is represented by the formula III and may have been formed by the condensation, *in situ*, of fructose dicarbonate with monocarbomethoxy fructose carbonate. Galactose, under similar conditions, gave rise to *tricarbomethoxy galactose carbonate* (IV) and as by-product, an isomeride. These galactose derivatives appear to belong to the 1 : 4-oxide series and not to the 1 : 5. With glucose the reaction introduced substituent groups of only one



(IV.)



(V.)



(VI.)

type. The product in this case was not crystalline and is represented by *tetracarbomethoxy glucose* (V). Mannitol gave rise to a completely substituted product, *dicarbomethoxy mannitol dicarbonate* (VI). Sucrose, on the other hand, yielded a hepta- or octa-carbomethoxy-derivative which displayed an unexpected stability towards 1 per cent. hydrochloric acid at 100°.

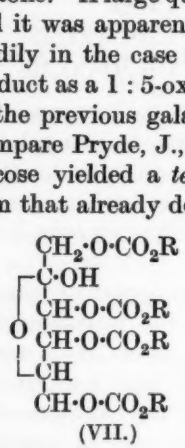
In the literature, the only reference to a compound of similar character to those indicated above describes the isolation of a completely substituted glucose derivative, prepared by Zemplén and Lászlo (*Ber.*, 1915, **48**, 921) in the course of their work on the condensation of sugars with acyl chlorides. These authors condensed glucose with chloroformic esters in presence of pyridine and obtained pentacarbomethoxy glucose and the corresponding ethoxy-derivative, which do not contain the cyclic carbonate linking (A) but are esters of the acid carbonate type (B).

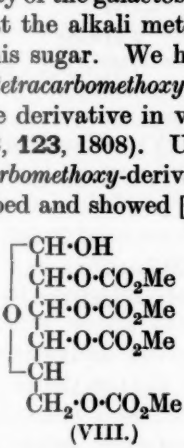
As a second method of preparation we also have adopted this procedure involving the use of pyridine as condensing agent. We have, however, adapted this reagent with the object of isolating, not the completely substituted sugars, but the partly substituted derivatives which we hope subsequently to use in further synthetic work.

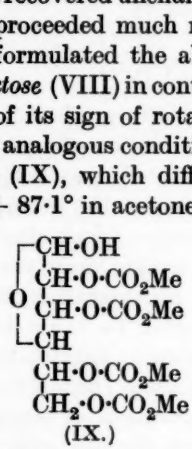
Applying this second method of condensation to the case of fructose, we isolated a *tetracarbomethoxy fructose*. This compound did not display ordinary mutarotation and therefore it would seem that the reducing group of the sugar was protected by a substituent group. Such an inference cannot be drawn with certainty, inasmuch as tetra-acetyl fructose does not show mutarotation although it readily gives rise to the corresponding fructoside (Hudson and Brauns, *J. Amer. Chem. Soc.*, 1915, **37**, 2743). On this analogy, the tetracarbomethoxy fructose is formulated as indicated by VII,

since we have been able to prepare the methylfructoside. A remarkable phenomenon was exhibited, however, in that the specific rotation varied according as the solution was kept in the light or the dark. On exposure to light, a lower reading previously recorded showed exaltation, and this value again fell on keeping the solution in a dark room. We intend to examine this anomaly more closely. The corresponding tetracarbethoxy fructose also was obtained.

The pyridine method applied to galactose gave a viscid product which showed $[\alpha]_D + 92{\cdot}6°$ and did not exhibit mutarotation in acetone. A large quantity of the galactose was recovered unchanged, and it was apparent that the alkali method proceeded much more readily in the case of this sugar. We have formulated the above product as a 1 : 5-oxidic *tetracarbomethoxy galactose* (VIII) in contrast to the previous galactose derivative in view of its sign of rotation (compare Pryde, J., 1923, **123**, 1808). Under analogous conditions, glucose yielded a *tetracarbomethoxy*-derivative (IX), which differed from that already described and showed $[\alpha]_D + 87{\cdot}1°$ in acetone.


(VII.)


(VIII.)


(IX.)

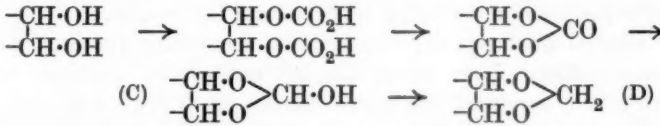
The use of silver oxide in place of dilute alkali or pyridine was tried in the case of fructose, but this led to fission of the sugar and α-methoxyacrylic acid, $CH_2{:}C(OMe){\cdot}CO_2H$, was identified as one of the products.

Evidence of the formation of definite carbonates of ethyl alcohol is contributed by Hempel and Seidel (*Ber.*, 1898, **31**, 2997), and confirmation of this reaction is furnished by Siegfried and Howwjanz (*Z. physiol. Chem.*, 1909, **59**, 376), who obtained calcium salts of a number of alcohols and sugars by passing carbon dioxide into excess of milk of lime containing the organic hydroxyl compound in solution at 0°. All the simpler alcohols were found to react, and also glycol, glycerol, erythritol, pentoses, hexoses, and the disaccharides lactose and maltose. The glycol derivative was the only one of these actually isolated and this has the constitution $\begin{matrix}CH_2{\cdot}O{\cdot}CO_2ca\\ CH_2{\cdot}O{\cdot}CO_2ca\end{matrix}$, but the other alcohols and sugars gave derivatives which were estimated analytically and some of these compounds could be precipitated by the addition of alcohol. These calcium salts of the

alcohols and sugar carbonates appeared to be all of the "acid carbonate" type, and decomposed on keeping or with gentle heat.

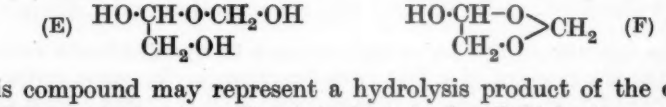
It therefore seems probable that changes analogous to the formation of sugar carbonates may occur in the plant accompanying the absorption of carbon dioxide by the leaf. There can be no doubt that sugars possess the capacity of combining with carbon dioxide, and it appears singular that no evidence is available pointing to the isolation of sugar carbonates from plants.

When it is considered, however, that such of these compounds of type B as we have prepared and investigated in the course of this work are almost insoluble in water or alcohol and are readily hydrolysed with dilute acids to the constituent sugars, it will be clear that the methods usually applied to the extraction of sugar derivatives from plant sources may have defeated any possible chance of the isolation of members of the carbonate class. Extending this view, it may well be that sugars, in common with numerous other plant products, possess the capacity, as does chlorophyll (Willstätter and Stoll, *Ber.*, 1917, **50**, 1791), of uniting with carbon dioxide to give definite additive compounds of the nature of acid or normal carbonates. These primary carbonates may quickly undergo reduction and ultimately appear as formal derivatives, illustrated by D:



The compounds C and D would yield respectively formic acid and formaldehyde on hydrolysis, and it is worthy of notice that Willstätter and Stoll (*loc. cit.*) proposed a scheme leading from the carbonic acid derivative of chlorophyll to these simple products. Many plant substances possess the type of grouping represented by D, for example, piperonal, and, moreover, Barger (J., 1908, **93**, 2081) has shown that the dioxymethylene group may easily be transformed into a cyclic carbonate linking.

Interesting experimental evidence from this point of view is afforded by the isolation, from the cabbage leaf, of a simple carbohydrate having the constitution (E) (Buston and Schryver, *Biochem. J.*, 1923, **17**, 470).



This compound may represent a hydrolysis product of the dioxymethylene derivative (F) of hydrated glycollaldehyde, or alter-

natively may be a condensation product of the latter with formaldehyde as the authors suggest. It may equally well have been formed through the carbonate grouping in either case.

Experimental.

Monocarbomethoxy Fructose Dicarbonate (II).—A mixture of 20 grams of fructose (1 mol.) in concentrated aqueous solution and 73·5 grams (7 mols.) of methyl chloroformate was cooled in a freezing mixture and stirred while 2*N*-sodium hydroxide (31 grams NaOH) was so added that the temperature remained at 0°. The syrup that separated was washed with water and with hot benzene, and the crystalline residue (4 grams) was dissolved in acetone, dried over magnesium sulphate, and recrystallised several times from a mixture of acetone and ether. On another occasion, the crude syrup was triturated with alcohol, and this was found to be the better method of isolation, since 15 grams of fructose yielded 6·7 grams of the crystalline derivative. The *dicarbonate* formed large, colourless prisms, m. p. 192°, $[\alpha]_D$ — 78·5° (in acetone; $c = 0{\cdot}82$) and —72·2° (saturated solution in ethyl acetate; $c = 0{\cdot}24$) (Found : C = 40·96, 41·42; H = 3·53, 3·84; OMe = 10·2, 10·9; *M*, in acetone = 270. $C_{10}H_{10}O_{10}$ requires C = 41·38; H = 3·45; OMe = 10·7 per cent.; *M* = 290). It reduced Fehling's solution * at 70° and gave barium carbonate on warming with barium hydroxide.

The alcohol washings deposited a semi-crystalline product, which was recrystallised from ethyl alcohol containing acetone, when 0·2 gram of a compound, colourless needles, m. p. 196°, was obtained which depressed the melting point of the main product and was strongly lævorotatory (Found : C = 41·63; H = 3·1; OMe = 6·4; *M*, by Rast's method, = 413, 431. $C_{17}H_{18}O_{16}$ requires C = 42·7; H = 3·8; OMe = 6·5 per cent.; *M* = 478).

These data indicate a difructose derivative (III) formed by the condensation of a fructose dicarbonate with a monocarbomethoxy fructose carbonate. The compound reduced Fehling's solution, but did not decolorise permanganate.

Tetracarbomethoxy Fructose (VII).—To a well-cooled mixture of 13·2 grams of fructose, 40·6 grams of dry pyridine, and 200 c.c. of chloroform, 48·5 grams of methyl chloroformate dissolved in 100 c.c. of chloroform were gradually added and the whole was shaken on the machine for several hours until the fructose had completely dissolved. The solution was concentrated under diminished

* The reduction of Fehling's solution cannot be regarded in this series as signifying the presence of a free reducing group in the sugar derivative, since heating with this alkaline reagent would tend to expose such a group by hydrolysis.

pressure, the residue washed with water until neutral, and the undissolved syrup triturated with cold alcohol, when 11 grams of an impure, crystalline substance remained. This was recrystallised several times from hot ethyl alcohol and squat, colourless prisms of *tetracarbomethoxy fructose*, m. p. 126—127°, were isolated (Found : C = 40·86; H = 5·18; OMe = 28·6, 29·5, 28·6; *M*, in acetone = 432. $C_{14}H_{20}O_{14}$ requires C = 40·77; H = 4·85; OMe = 30·1 per cent.; *M* = 412). Methylation with Purdie's reagent gave, after two treatments, the corresponding methyl fructoside, but further treatment with methyl chloroformate and pyridine resulted in the recovery of the compound unchanged. Although almost insoluble in cold water, it dissolved appreciably in hot water, from which, on cooling, small, pentagonal plates of unchanged melting point crystallised. The compound reduced Fehling's solution with comparative ease at 70°, and the substituent groups were removed on warming with baryta. Polarimetric data were recorded showing $[\alpha]_D$ — 75·1° (*c* = 2·47), —77·6° (*c* = 2·04) in acetone and —98·1° (*c* = 1·44) in chloroform. On keeping these acetone and chloroform solutions in sunlight or in the dark, at a constant temperature, anomalous variations in the rotation values were observed. In alcohol containing 5 per cent. of hydrochloric acid the reading was $[\alpha]_D$ — 80·6° (*c* = 0·62) and this value remained permanent until the solution was heated at 80°, when it underwent the following changes :

Time in hours	½	1	4	6	9	11	18	24
$[\alpha]_D$	—71·5°	—75°	—55°	—24·5°	—35°	—6·5°	—5°	—3·5°

Tetracarbethoxy Fructose (VII).—The corresponding carbethoxy-derivative was similarly prepared from 13·2 grams of fructose, 31·6 grams of pyridine, and 48 grams of ethyl chloroformate. A syrup (19 grams) was isolated (Found : C = 46·82; H = 5·84; OEt = 34·3; *M* = 494. $C_{18}H_{28}O_{14}$ requires C = 46·16; H = 5·98; OEt = 38·5 per cent.; *M* = 468) which crystallised after a year. By slow evaporation of a solution of the solid in alcohol–ether, and scratching, impure crystals were obtained which, washed with cold alcohol and recrystallised several times from this solvent, yielded pure *tetracarbethoxy fructose*, m. p. 118°, $[\alpha]_D$ —97·0 to —95·3° in chloroform (*c* = 1·6) and —72·0° in acetone (*c* = 0·6) (Found : C = 46·02; H = 6·1; OEt = 32·4 per cent.).

In subsequent preparations, the difficulty of crystallisation was minimised by nucleation, and from 10 grams of fructose 8·8 grams of crude, crystalline product, slightly soluble in ether, were obtained along with 14·5 grams of a straw-yellow syrup which was readily soluble in ether and reduced neutral permanganate instantaneously in the cold. The syrup was extracted twice with 20 c.c. of hot ether,

the solution decolorised with charcoal, and evaporated under diminished pressure, yielding 5·2 grams of an *isomeride* of tetracarbethoxy fructose, a faintly yellow syrup, $[\alpha]_D$ −19° in acetone ($c = 2·4$), which reduced Fehling's solution, but permanganate not so pronouncedly (Found : C = 46·16; H = 5·7 per cent.).

Tricarbomethoxy Galactose Carbonate (IV).—As in the preparation of monocarbomethoxy fructose dicarbonate, galactose (20 grams) was condensed with methyl chloroformate (73·5 grams) in presence of 2*N*-alkali (275 c.c.) at 0°. The syrup was extracted with both cold and hot benzene. In a dry acetone solution of the residue, after addition of ether, semi-crystalline deposits formed slowly and these were collected over several months. The earlier deposits, purified by recrystallisation from acetone–ether, gave rise to *tricarbomethoxy galactose carbonate*, flocculent masses of colourless needles, m. p. 170·5—171°, $[\alpha]_D$ − 88·9° in acetone ($c = 0·53$) (Found : C = 40·69; H = 4·44; OMe = 23·5. $C_{13}H_{16}O_{13}$ requires C = 41·05; H = 4·21; OMe = 24·5 per cent.). The later deposits gave this compound and also an *isomeride*, which, purified by means of ethyl alcohol, was obtained as a colourless, amorphous powder, m. p. 126°, $[\alpha]_D$ from −29·8° to −45° in acetone ($c = 0·40$) and −34·9° in chloroform ($c = 1·1$); the rotations showed variations according as the solutions were kept in the light or the dark (Found : C = 41·12; H = 4·16; OMe = 22·1; *M*, by Rast's method, = 397. Calc., *M* = 380). The two isomerides in admixture melted at an intermediate temperature. Both reduced permanganate in alkaline aqueous solution, but not in cold acetone, and both reacted with barium hydroxide solution to give barium carbonate. The compound, m. p. 126°, is the more soluble in alcohol.

Tetracarbomethoxy Galactose (VIII).—When pyridine was used as condensing medium, the reaction between galactose and methyl chloroformate proceeded with extreme difficulty, 10 grams of finely-sieved galactose appearing unchanged after some hours' shaking. Agitation was continued for another day after further addition of reagents and the mixture was then filtered; 6·2 grams of unchanged galactose were recovered and the filtrate yielded 4·0 grams of a yellow glass (Found : C = 40·62; H = 4·8; OMe = 27·8. Tetracarbomethoxy galactose, $C_{14}H_{20}O_{14}$, requires C = 40·77; H = 4·85; OMe = 30·1 per cent.); $[\alpha]_D$ in acetone = + 92·6° ($c = 1·86$). No mutarotation was observed.

Tetracarbomethoxy Glucose (V).—Glucose (10 grams), dissolved in a small volume of water, was treated at 0° with methyl chloroformate (37 grams) and 194 c.c. of 2*N*-sodium hydroxide; after the addition of 84 c.c. a syrup began to separate and the solution

remained permanently alkaline. The syrup was dried in acetone with magnesium sulphate, the solvent removed under diminished pressure, and the viscid product heated at 100° under 15 mm. for 2 hours; on cooling, it congealed to an amber-coloured glass (13 grams) (Found: C = 40·96; H = 4·65; OMe = 27·1, 27·5; *M*, in acetone, = 402. $C_{14}H_{20}O_{14}$ requires C = 40·77; H = 4·85; OMe = 30·1 per cent.; *M* = 412). It was purified by solution in benzene and precipitation with light petroleum. The rotation data recorded were as follows: in ethyl alcohol, $[\alpha]_D = +34·6°$ and $+34·1°$ for $c = 1·56$ and 0·73, respectively (preparation A); in acetone, $[\alpha]_D = +34·8°$ for $c = 0·52$ (prep. B) and $+51·3°$ for $c = 2·2$ (prep. C).

The tetracarbomethoxy glucose was methylated with Purdie's reagent and yielded vitreous *tetracarbomethoxy methyl glucose* (Found: OMe = 33·9. Calc., 36·4 per cent.). Difficulty was experienced in distilling this product, which was very viscid.

Zemplén and László (*loc. cit.*) have prepared a crystalline pentacarbomethoxy β-glucose, m. p. 122°, $[\alpha]_D + 1·35°$ in chloroform, by condensing β-glucose with methyl chloroformate in presence of pyridine; also the corresponding carbethoxy-derivative is described, m. p. 102°, $[\alpha]_D + 2·47°$. We have not isolated these fully substituted products, but have obtained a different *tetracarbomethoxy glucose* (IX) from that described above by the use of these reagents and this shows $[\alpha]_D + 87·1°$ in acetone (Found: OMe = 27·3. $C_{14}H_{20}O_{14}$ requires OMe = 30·1 per cent.). The percentage values of carbon and hydrogen are insufficient in themselves to differentiate between the compounds containing four or five carbomethoxy-groups, but the methoxyl values are more diagnostic. The product reduced Fehling's solution, and gave a precipitate of barium carbonate on warming with baryta and of sodium carbonate with alcoholic sodium hydroxide.

Dicarbomethoxy Mannitol Dicarbonate (VI).—This substance, like the fructose and galactose carbonates, was prepared in aqueous alkaline medium from mannitol (10 grams), methyl chloroformate (41·7 grams), and 2*N*-sodium hydroxide (19 grams NaOH). The syrup was dried in acetone and heated for some time under diminished pressure. Yield 5·4 grams (Found: C = 41·19; H = 4·26; OMe = 17·65; *M*, in acetone, = 344. $C_{12}H_{14}O_{12}$ requires C = 41·15; H = 4·0; OMe = 17·7 per cent.; *M* = 350). *Dicarbomethoxy mannitol dicarbonate* is a yellow gum which has no effect upon Fehling's solution and shows $[\alpha]_D + 29·6°$ in acetone ($c = 1·2$).

Action of Methyl Chloroformate on Sucrose.—Ten grams of sucrose and 40 grams of pyridine were treated with 50 grams of methyl

chloroformate in the usual manner. After shaking for 2 hours, the greater part of the sucrose had not reacted and little more dissolved after a further addition of reagents and prolonged agitation. From the filtered solution there were obtained 2·0 grams of a pale yellow glass, which was dried in a high vacuum at 100° [Found: C = 41·61; H = 4·61; OMe = 26·8. (*a*) $C_{26}H_{35}O_{25}$ requires C = 41·78; H = 4·81; OMe = 29·02 per cent. (*b*) $C_{28}H_{37}O_{27}$ requires C = 41·69; H = 4·72; OMe = 30·8 per cent. The formulæ (*a*) and (*b*), respectively, indicate the hepta- and octa-substituted derivatives]. $[\alpha]_D = +53·8°$ in acetone ($c = 1·0$). The compound did not reduce Fehling's solution and even after boiling with 1 per cent. hydrochloric acid for 1 hour or 5 per cent. hydrochloric acid for ¼ hour there was no reduction, although in the latter case when the treatment was maintained for 1 hour some slight reduction became evident.

Ethylene Carbonate (I).—Vigorous reaction occurred between the disodium derivative of ethylene glycol (prepared from 12·4 grams of the glycol and 9·2 grams of sodium) and methyl chloroformate (38 grams) in dry ether. After 12 hours, the mixture was heated on a water-bath for 1 hour, the solution decanted, and united with several ether extracts of the residue, the solvent was evaporated, and the residue fractionated. The main fraction, b. p. 116—119·5°/16 mm., solidified, on cooling, to a crystalline mass, m. p. 33—36°. Yield 7 grams. The substance was purified by recrystallisation from alcohol and finally from ether, when ethylene carbonate crystallised in colourless plates, m. p. 38·5°, b. p. 238—238·5° (Found: C = 40·79; H = 4·24; *M*, in acetone, = 77 and by the cryoscopic method in acetone, 100. Calc., C = 40·91; H = 4·55 per cent.; *M* = 88). Nemirowsky (*loc. cit.*) gives m. p. 38·5—39° and b. p. 236°.

Attempted Carbomethoxylation of Glycol by means of the Silver Oxide Method.—To a mixture of 5·0 grams of glycol and 20 grams of methyl chloroformate, silver oxide was added in small quantities, the mixture being well shaken. When the vigour of the reaction had subsided, ether was added and the whole was heated under reflux for 3 hours. After filtration and removal of the solvent, the residue was fractionated twice under diminished pressure and 2·4 grams of a colourless liquid were obtained, b. p. 119—121°/14 mm. This proved to be a mixture, but after nucleation with a crystal of ethylene carbonate and cooling in ice it partly solidified; the crystals, m. p. 34·5—37° after recrystallisation, did not depress the melting point of ethylene carbonate.

Application of the Silver Oxide Method to Fructose.—Reaction between 6·0 grams of fructose, 22 grams of methyl chloroformate,

and 23 grams of silver oxide in dry ethyl acetate commenced after slight warming and persisted spontaneously for ½ hour. The mixture was heated for 4 hours, when a further quantity of reagent was added (half the initial amounts). After heating for a further 2 hours, followed by decoloration with charcoal, the solution was concentrated to a brown gum. On distillation, the first fraction came over between 55° and 80°, but the main portion was collected at 65—75°/12 mm. as a colourless liquid, strongly acid in character, which reduced both permanganate and Fehling's solution in the cold, and was optically inactive. This appeared to be α-methoxyacrylic acid (Found: C = 46·89; H = 5·98. Calc. for $C_4H_6O_3$, C = 47·06; H = 5·88 per cent.).

The authors are indebted to Mr. J. M. Smith for some of the molecular-weight determinations and to the Chemical Society for a grant for the purchase of materials.

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NEWCASTLE-UPON-TYNE. [*Received, March 8th*, 1924.]

CLI.—*The Photochemistry of the Halogen Hydrides.*

By EDMUND JOHN BOWEN.

THE experimental observations on the photochemical relationships of hydrogen with the halogens are peculiarly complex, and have not been completely interpreted in terms of a common explanation. There are two views of the mechanism of the primary photochemical processes. One is that a dissociation into atoms occurs, *e.g.*,

$$Cl_2 + h\nu \longrightarrow Cl + Cl$$
$$HI + h\nu \longrightarrow H + I,$$

and the other is that "activated" molecules are formed which are capable of chemical reaction. It has hitherto not been possible to decide between these two views. The first has been used tentatively with success in explaining certain observations on the photochemical behaviour of the halogens by Nernst (*Z. Elektrochem.*, 1918, **24**, 335), by Nernst and Noddack (*Sitzungsber. Preuss. Wiss. Berlin*, 1923, 110), and by Warburg (*ibid.*, 1916, 314; 1918, 300). The purpose of this paper is to show that the "dissociation" view first elaborated by Nernst is capable of giving a quantitative explanation of all the experimental observations on the photochemistry of the halogens if it is developed consistently from the thermochemical heats of reaction.

The following heats of reaction are obtained from the most recent

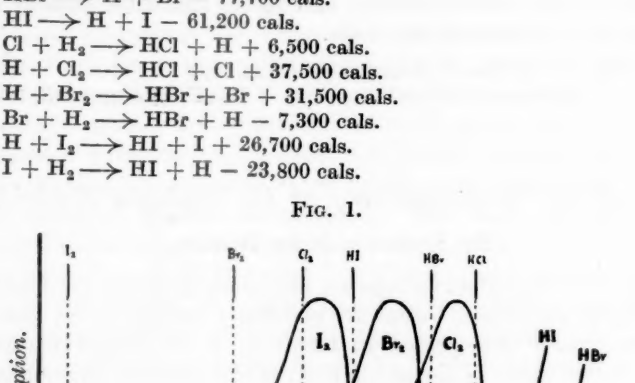
work; the least certain is probably the heat of dissociation of chlorine, for a discussion of which reference should be made to the original paper.

(1) $Cl_2 \longrightarrow Cl + Cl - 54{,}000$ cals. (Henglein, *Z. anorg. Chem.*, 1922, **123**, 137).
(2) $Br_2 \longrightarrow Br + Br - 46{,}200$ cals. (Henglein, *loc. cit.*).
(3) $I_2 \longrightarrow I + I - 34{,}500$ cals. (Henglein, *loc. cit.*).
(4) $H_2 \longrightarrow H + H - 85{,}000$ cals. (Langmuir, *J. Amer. Chem. Soc.*, 1912, **34**, 860; *Z. Elektrochem.*, 1917, **23**, 217; Isnardi, *ibid.*, 1915, **21**, 405; Franck, Knipping, and Krüger, *Ber. deut. physikal. Ges.*, 1919, **21**, 728).
(5) $H_2 + Cl_2 \longrightarrow 2HCl + 44{,}000$ cals. (Thomsen, "Therm. Unt.").
(6) $H_2 + Br_2 \longrightarrow 2HBr + 24{,}300$ cals. „ „ „ „
(7) $H_2 + I_2 \longrightarrow 2HI + 2{,}900$ cals. (Nernst, *Z. Elektrochem.*, 1909, **15**, 687).

From these the heats of reactions below follow :

(8) $HCl \longrightarrow H + Cl - 91{,}500$ cals.
(9) $HBr \longrightarrow H + Br - 77{,}700$ cals.
(10) $HI \longrightarrow H + I - 61{,}200$ cals.
(11) $Cl + H_2 \longrightarrow HCl + H + 6{,}500$ cals.
(12) $H + Cl_2 \longrightarrow HCl + Cl + 37{,}500$ cals.
(13) $H + Br_2 \longrightarrow HBr + Br + 31{,}500$ cals.
(14) $Br + H_2 \longrightarrow HBr + H - 7{,}300$ cals.
(15) $H + I_2 \longrightarrow HI + I + 26{,}700$ cals.
(16) $I + H_2 \longrightarrow HI + H - 23{,}800$ cals.

FIG. 1.



The absorption spectra of the halogens and of the halogen hydrides are roughly plotted in Fig. 1. Large portions of these spectra are actually composed of closely packed, sharp lines, and the curves are only intended to represent mean extinctions over not too narrow ranges of wave-length. The wave-lengths corresponding to the heats of dissociation into atoms of the halogens and of the halogen hydrides, calculated from equations (1), (2), (3), (8), (9), (10), by the relation $Q = Nh\nu$, are indicated on the diagram. The values are :

Cl_2.	Br_2.	I_2.	HCl.	HBr.	HI.
5220	6100	8170	3080	3630	4610 Å.

The "dissociation" theory, as distinguished from the "activation" theory, is shown below to interpret experimental results in a remarkable manner, and to make predictions which can be verified. The method may be summarised as follows:

The relative positions of these limits and of the range of wave-lengths absorbed will determine whether the quantum of energy is large enough to dissociate the molecule into atoms. Whether these atoms can combine with hydrogen depends on the heats of reaction (11), (14), and (16). At wave-lengths longer than the limiting ones for the halogen hydrides combination will either be complete or will not occur at all, because of the impossibility of reactions (8), (9), (10); and whether secondary reaction "chains" will be set up depends on the heats of those reactions such as (12) and (13). The assumption is made that a large heat evolution makes a reaction between atoms occur spontaneously, while negative heats make a reaction occur with difficulty, if at all.

Photochemical decomposition of the halogen hydrides will only take place in light of wave-lengths shorter than the limiting ones in the above table. Above these limiting values, states of photochemical equilibrium will be expected, the position of the equilibrium depending on the heats of reaction and on the relative absorptions of the halogen and its hydride. In certain cases, this may lead practically to complete hydride decomposition; and the rate of this can be determined.

Applying these considerations in detail to the actual cases, we suppose that chlorine molecules, absorbing quanta of wave-length shorter than 5220 Å., will be dissociated into atoms. Because of the large heat of reaction (11), these will be capable of forming hydrogen chloride; and because of the large heat of (12) the rate will be many times faster than that given by the photochemical equivalence law, owing to the persistence of (11) and (12) as a chain of "dark" reactions (Nernst, *loc. cit.*). Experimentally, mixtures of hydrogen and chlorine have been prepared in which 10^6 molecules of hydrogen chloride have been formed for each quantum of blue light absorbed; and the actual existence of the "chains" seems to be shown by the work of Weigert and Kellerman (*Z. physikal. Chem.*, 1923, **107**, 1).

The view that atoms are concerned in the reaction explains the effect of water vapour. Bodenstein and Dux (*ibid.*, 1913, **85**, 297) found no difference in the rate of change with partial pressures of water vapour varying between 0·004 mm. and 2·3 mm. This shows that water takes no part in the chain reactions. On the other hand, Tramm (*ibid.*, 1923, **105**, 356), drying the gases by high vacuum and low temperature technique, and avoiding the uncertainty due

to the introduction of "inhibitors" from drying agents, found that they did not react in light. His experiments, however, were only comparative and combination may have been occurring at a rate faster than that of Einstein's law and yet have been undetected. The explanation seems to be completely analogous to that given by Wood (*Proc. Roy. Soc.*, 1922, [*A*], **102**, 1) of the effect of water vapour on the production of hydrogen atoms in vacuum tubes. In a clean, dry vessel the high catalytic activity of the walls will keep down the concentration of the atoms and cut off the length of the "chains"; in a moist vessel the walls are poisoned and do not interfere with the homogeneous reaction. This view can be extended to explain the enormous effect of traces of nitrogen trichloride in inhibiting this reaction (Chapman and Burgess, J., 1906, **89**, 1399), if it be assumed that this substance, when adsorbed on glass, or otherwise, readily reacts with hydrogen and chlorine atoms.

At wave-lengths shorter than 3080 Å., hydrogen chloride will be expected to be decomposed, but because of its small absorption compared with that of chlorine and of the large heat evolutions of reactions (11) and (12) this will not be appreciable until short wave-lengths are reached. Coehn and Stuckardt (*Z. physikal. Chem.*, 1916, **91**, 722) found a state of photochemical equilibrium at wave-lengths less than 2200 Å.

Bromine will be dissociated into atoms at wave-lengths shorter than 6100 Å. Owing to the small negative heat of reaction (14) these will be capable of reacting with a hydrogen molecule only occasionally, if at all. The combination, however, at wave-lengths longer than 3630 Å., where hydrogen bromide dissociates, will be complete if it does take place. The number of atoms combining will be less than the number of quanta absorbed, and a rise of temperature would greatly increase the yield, because a little thermal activation would be expected to make a much larger fraction of the bromine atoms able to attack a hydrogen molecule. This is in agreement with the observed facts. The photochemical combination has been found to be complete, but proceeding at a rate always less than that given by Einstein's law (Pusch, *Z. Elektrochem.*, 1918, **24**, 336), and to be remarkably affected by temperature (Lind, *J. Physical Chem.*, 1924, **28**, 55).

Beyond 3630 Å., a state of photochemical equilibrium will be expected, and at very short wave-lengths, where the hydrogen bromide absorption dominates, complete decomposition of this gas. Because of the large negative heat of the reaction

$$Br + HBr \longrightarrow H + Br_2 - 31{,}500 \text{ (inverse of 13)}$$

bromine atoms cannot interfere with the decomposition of hydrogen bromide, and one quantum will decompose 2 mols., the reactions

involved being (9) and (13), other reactions being inadmissible. These deductions are in exact agreement with the work of Coehn and Stuckardt and of Warburg (*loc. cit.*).

Owing to the large negative heat of the reaction

$$I + H_2 \longrightarrow HI + H - 23{,}800 \quad (16)$$

iodine will not be expected to combine with hydrogen, except at very short wave-lengths, where the atoms will possess considerable energy. Coehn and Stuckardt found the beginning of an equilibrium state at wave-lengths shorter than 2200 Å. At wave-lengths longer than this, they could discover no combination. To avoid the possibility that in these experiments decomposition of hydrogen iodide was taking place, this was further tested experimentally. A number of small glass bulbs containing a little iodine were filled with hydrogen, purified in the usual manner from oxygen and water vapour. These were exposed for several days to sunlight passed through red, orange, and green filters. These wave-lengths are shown below to be ineffective in decomposing hydrogen iodide. The bulbs were broken under conductivity water and the electrical resistance of the solutions was measured. No formation of hydrogen iodide could be detected greater than 1 part in 10,000 parts.

Hydrogen iodide is known to be decomposed by visible light. On these views, it should not be decomposed by light of wave-lengths greater than 4610 Å. To test this, pure hydrogen iodide was generated by dropping a strong aqueous solution, prepared by treating a solution of sodium iodide with metaphosphoric acid and filtering, on to phosphorus pentoxide in an all-glass apparatus, previously evacuated. The gas was sealed in small bulbs which were exposed to sunlight behind filters of copper and calcium chloride solutions (Jones and Uhler, *Amer. Chem. J.*, 1907, **37**, 126), the edges of the absorption band varying in the different filters from the violet to the green. It was found that no decomposition occurred in those bulbs exposed to light passing filters with absorption band edges of wave-length greater than 4500 Å.

Because of the large negative heat of the reaction

$$HI + I \longrightarrow I_2 + H - 26{,}700 \text{ (inverse of 15)}$$

iodine will not act as a photocatalyst in the decomposition of hydrogen iodide, as has been suggested (Plotnikov, "Lehrbuch der Photochemie," p. 388). This can be shown to be in agreement with the work of Bodenstein (*Z. physikal. Chem.*, 1897, **22**, 23), who found that the rate of photochemical decomposition of hydrogen iodide in visible light varied directly as its partial pressure. This would be expected if the hydrogen iodide was the absorbing substance with weak absorption, whilst if the iodine absorbed the light the rate would have been always constant, because the iodine vapour

was saturated in the experiments. Further, iodine absorbs in the green, and hydrogen iodide is not decomposed by light of this spectral region.

In the case of the decomposition of hydrogen iodide, for the same reasons as are discussed in that of hydrogen bromide, an explanation is afforded of the results of Warburg with regard to the application of the law of the photochemical equivalence.

The dissociation hypothesis thus affords a fairly complete explanation of the complex photochemical relationships of hydrogen with the halogens.

These results are not in conflict with work on the mechanism of the physical process of light absorption (compare Gerlach, *Physikal. Z.*, 1923, **24**, 467). The important chemical fact is that the heats of dissociation of the halogens appear to be less than the energy changes of these processes. There remains the question, however, of the possibility of dissociation into ions instead of into atoms. The heats of the processes $HX \longrightarrow H^+ + X^-$ for the halogen hydrides, as determined by the ionisation potential and in other ways, are of the order of 300,000 cals. (Knipping, *Z. Physik*, 1921, **7**, 328), and therefore such dissociation cannot take place in ordinary photochemical work. The heats of ionisation Halogen $\longrightarrow$ ion$^+$ + ion$^-$ are unknown; whether dissociation will take place in this way instead of into atoms depends on the unknown magnitudes of the heats of the processes Atom $-$ electron $\longrightarrow$ ion$^+$ compared with those of the known processes Atom + electron $\longrightarrow$ ion$^-$ (electron affinities). In view of the possibility that the primary process of light absorption of the halogens may be Mol. $\longrightarrow$ mol.$^+$ + electron, it is important to note that the reactions Mol. + electron $\longrightarrow$ atom + ion$^-$ are exothermic (Fajans, *Ber. Deut. physikal. Ges.*, 1919, **21**, 723). The necessary modifications of the hypothesis of this paper due to the possible formation of ions cannot adequately be discussed until the unknown energy changes have been determined.

The experiments of Wood and Franck (*Phil. Mag.*, 1911, [vi], **21**, 261, 265, 309) on the fluorescence of halogen vapours at low pressures show that "excited" molecules can exist under certain conditions; but the work of Dunoyer (*Le Rad.*, 1913, **10**, 400) and of Stern and Volmer (*Physikal. Z.*, 1919, **20**, 183) shows that the average life of such molecules is less than 10^{-6} sec.; that is, they do not survive one collision. This work cannot therefore be taken as contrary to the views expressed in this paper.

Summary.

It is shown that the "dissociation" theory of the photochemical combination of the halogens with hydrogen and of the decomposition

of the halogen hydrides leads to a fairly complete interpretation of the numerous results, whilst the "activation" theory is incapable of these interpretations.

This result is not at variance with work on the actual physical process of light absorption.

I am glad to acknowledge the valuable criticism of Professor F. A. Lindemann and of Dr. N. V. Sidgwick.

UNIVERSITY COLLEGE, OXFORD. [*Received, March 1st*, 1924.]

CLII.—*The Properties of Ammonium Nitrate. Part VIII. Analysis of Crystalline Deposits from Solution in Fused Ammonium Nitrate.*

By EDGAR PHILIP PERMAN and DAVID RICHARD DAWKINS.

THE deposits formed on cooling fused salts are usually so finely divided that it is extremely difficult to separate them from enclosed mother-liquor. Previous attempts have been made to effect this by filtration, but without much success (Cady, *J. Physical Chem.*, 1899, **3**, 127; Van Eyk, *Z. physikal. Chem.*, 1899, **30**, 430). Stead found (*J. Soc. Chem. Ind.*, 1914, **33**, 181) that in the accidental very slow cooling of a pig-iron, the ternary eutectic iron–silicon–phosphorus was almost entirely squeezed out by the external pressure produced on the inside mass.

In order to settle the equilibrium data for ammonium nitrate and other salts, described in Parts IV—VII, it was essential to analyse such deposits, as in certain cases the curves were difficult to interpret. Three methods were employed before a satisfactory separation was effected: (1) centrifugal method, (2) filtration, (3) filtration followed by treatment in a screw press.

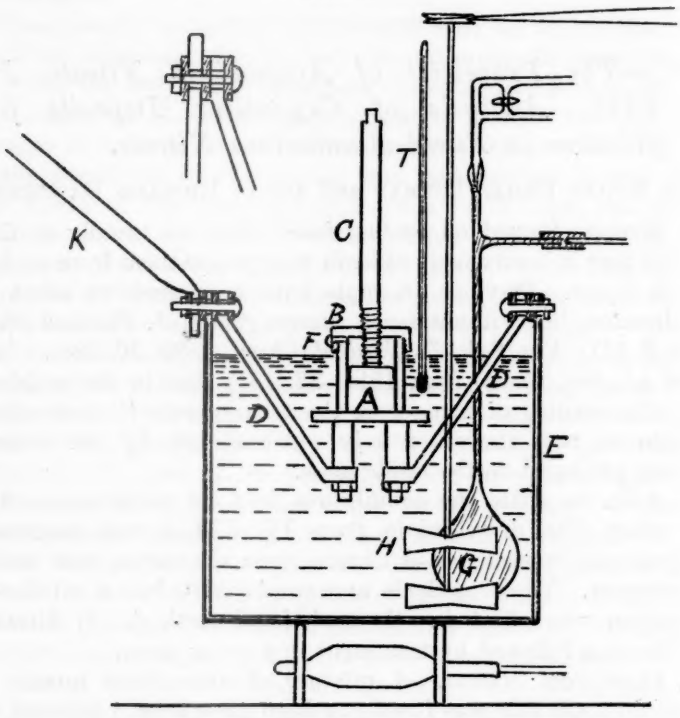
1. *Centrifugal Method.*—A mixture of ammonium nitrate and ammonium chloride was fused in a hard glass tube, protected with cotton wool or other insulating material, and immediately centrifuged. After cooling, portions of the salt mixture, taken from different parts of the block, were analysed by means of standard silver nitrate solution. With a velocity of 10,000 revolutions per minute, a considerable amount of separation was effected, but it was not considered advisable to pursue the method further, especially owing to the difficulty of regulating the temperature.

2. *Filtration.*—A Gooch filter was fitted up in an air-bath, and connected on one side with a Fleuss pump and on the other with a second air-bath. In an experiment with a mixture of ammonium

nitrate and ammonium chloride, the filter was maintained at a temperature 10° below its initial freezing point, and the other air-bath 20° above the freezing point. Hot air was pumped over the filter for about 3 minutes. Analysis showed that the separation of solid and liquid was very imperfect.

In order to determine the quantity of mother-liquor retained by the crystals, control experiments were made with powdered glass of about the same fineness as the crystals, the temperature being

FIG. 1.



kept several degrees above the freezing point of the mixture of salts. Analyses showed that from 32·45 to 46·77 per cent. of the residue on the filter consisted of mother-liquor, so that it was impossible to correct the original results obtained by filtration for this error.

3. *Filtration followed by the Use of a Screw Press.*—A small steel cylinder, *A* (internal diameter 1 inch, height 1·5 inches) was fitted with a screw-cap, *B*, through which passed the central rod of a plunger, *C*. The cylinder was supported securely by strips, *DD*, bolted to the upper edge of the oil-bath, *E*. The shaded portions in the diagram represent asbestos washers. The holes in the strip

and the side of the bath through which the bolt passes were made considerably larger than the bolt itself. In this way, the strips, *DD*, did not make contact with the metal bath at any point. A small screw, *F*, prevented the lid from rotating when the plunger was set in motion. The temperature of the oil-bath was kept constant within 2° by the regulator, *G*. The oil was stirred vigorously by the stirrer, *H*, which was driven by an electro-motor. The handle, *K*, attached to the bath was held firmly and so prevented any movement of the latter during the process of pressing. The thermometer, *T*, the bulb of which was situated close to the cylinder, at the same level as the solid within the press, recorded a temperature that agreed within 1° with the temperature inside the cylinder.

Procedure.—A mixture of ammonium nitrate and ammonium chloride was prepared, cooled, and filtered on the Gooch crucible as in method (2); a perforated disk of aluminium foil, placed on the glass-wool in the crucible, protected the solid from contamination with the glass-wool. The solid from the Gooch crucible was transferred to the cylinder of the screw-press. At the bottom of the cylinder were placed several disks of asbestos cardboard, above these a disk of aluminium foil, then the solid to be pressed, next another aluminium disk, and at the top several disks of asbestos. The plunger and the screw cap were adjusted, and the oil-bath was heated to a suitable temperature. The plunger was screwed down tightly, so that the solid inside the cylinder was subjected to a high pressure. The liquid portion was squeezed out and absorbed by the asbestos.

After one pressing, the apparatus was disconnected and a portion of the solid removed for analysis. The remainder was powdered, dried, and subjected to another pressing, using fresh aluminium and asbestos disks. The pressing operations were repeated whilst the temperature was slowly raised (being kept, however, well below the melting point of ammonium nitrate) until no more liquid could be pressed out.

Tests of the Method.—Initial mixture contained 4·95 per cent. NH_4Cl. Solid retained by Gooch crucible contained 4·47 per cent. NH_4Cl. Crystallising point 158°. Air-bath 153°. Air-chamber 175°. The solid from the filter was divided into two portions and these were pressed separately. t = max. temp. of the oil-bath.

	Portion I.		Portion II	
	% NH_4Cl.	t.	% NH_4Cl.	t.
Solid after 1 pressing	3·29	141°	3·10	143°
,, 2 ,,	3·25	150	2·84	143·5
,, 3 ,,	3·22	160	None melted	141·5
,, 4 ,,			,, ,,	146
,, 5 ,,			2·49	155

It is impossible theoretically for *pure* ammonium nitrate to separate and the analytical results agree closely with what would be expected.

The results obtained on the other side of the eutectic are even better :—

	Initial mixture contained 14·77% NH_4Cl. Solid retained by the Gooch 39·40% NH_4Cl. Crystallising point 168°. Air-bath 152°. Air-chamber 175°.		Initial mixture contained 15·02% NH_4Cl. Solid retained by the Gooch 24·85% NH_4Cl. Crystallising point 174°. Air-bath 150°. Air-chamber 175°.	
	% NH_4Cl.	*t*.	% NH_4Cl.	*t*.
Solid after 1 pressing	Not analysed	143·5°	35·88	141°
,, 2 ,,	81·68	160	80·54	140·5
,, 3 ,,	None melted	149·5	98·97	142
,, 4 ,,	95·61	163		

After the third pressing, the solid was slightly contaminated with asbestos, but contained, nevertheless, close on 99 per cent. of ammonium chloride. These tests show that the combination of filtration and pressing makes an effective method for analysing the crystalline deposits obtained.

Application of the Method.—This method has been applied to confirm the decisions arrived at from a consideration of the melting-point curves in Parts IV—VII :—

(*a*) *Part IV* (J., 1922, **121**, 2478). Ammonium nitrate and sodium chloride.

Area.	$\frac{Cl}{Cl + NO_3}$.	$\frac{Na}{Na + NH_4}$.	Number of pressings.	% of salt found.
NH_4NO_3	0·112	0·051	4	97·4
,,	0·101	0·092	5	96·4
NH_4Cl	0·185	0·130	5	97·9
,,	0·131	0·131	4	97·4
,,	0·125	0·172	4	98·7
$NaNO_3$	0·070	0·251	3	97·2
NaCl	0·149	0·230	3	96·6

The numbers given represent minimum values and show from 1 to 3 per cent. of mother-liquor and other impurities (such as a trace of asbestos). In many cases, a number of analyses were made at different stages of the experiments, and a gradual approach to these high percentages was obtained, thus indicating the separation of a pure substance. The values obtained in the ammonium chloride area appear to dispose of the idea of a double salt in the lower portion, as has been suggested.

(*b*) *Part V* (J., 1923, **123**, 846). Ammonium nitrate and potassium chloride.

Area.	$\frac{Cl}{Cl + NO_3}$.	$\frac{Na}{Na + NH_4}$.	Number of pressings.	% of salt found. NH_4NO_3.	KNO_3.
NH_4NO_3	0·081	0·061	4	97·7	—
NH_4NO_3 and KNO_3	0·102	0·155	5	55·4	44·6
	0·089	0·192	4	57·2	42·8
NH_4Cl	0·168	0·050	4	NH_4Cl 98·5	
	0·150	0·171	6	NH_4Cl 94·2	

The last number given is the least satisfactory, but as the percentage rose rapidly during the pressing (being 59·3 after the third pressing) it appears to indicate a deposit of ammonium chloride.

The experiments in the mixed-crystal area gave mixtures of ammonium nitrate and potassium nitrate, as would be expected. The proportion between the two salts separating is also given roughly, but it is possible that this might alter during the pressing operations. The experiments appear to prove definitely that two salts separate together and they confirm strongly the conclusions drawn from the freezing-point curves.

(*c*) *Part VI* (J., 1923, **123**, 2131). Ammonium nitrate and potassium sulphate.

Area.	$\frac{SO_4}{SO_4 + 2NO_3}$.	$\frac{K}{K + NH_4}$.	% of salt found. $(NH_4)_2SO_4$.	NH_4NO_3.
Mixed crystals of NH_4NO_3 and $(NH_4)_2SO_4$.	0·030	0·062	32·0	68·0
" " "	0·030	0·086	33·9	66·1
" " "	0·012	0·096	11·3	88·7
Mixed crystals of $(NH_4)_2SO_4$ and K_2SO_4.			$(NH_4)_2SO_4$.	K_2SO_4.
" " "	0·063	0·146	64·7	30·4
" " "	0·067	0·130	74·3	21·4
" " "	0·021	0·128	72·1	20·0
" " "	0·019	0·117	74·9	20·1
Mixed crystals of NH_4NO_3 and KNO_3.	0·025	0·165	NH_4NO_3 53·3; KNO_3 46·7	

The remarks made in section (*b*) apply here also.

In the deposit from the first area little infusible residue was found, and therefore the ammonium nitrate was estimated by difference. The proportion of sulphate is smaller near the base line, as would be expected.

The ammonium nitrate in the third area also was obtained by difference, very little sulphate being present.

There is a deficiency in the results for mixed crystals of ammonium and potassium sulphates. Most of this is accounted for by the difficulty of squeezing out the mother-liquor. It is possible, however, that a small proportion of nitrate separates in this area.

(*d*) *Part VII* (this vol., p. 364). Ammonium nitrate and sodium sulphate.

Area.	$\frac{SO_4}{SO_4 + 2NO_3}$.	$\frac{Na}{Na + NH_4}$.	% of salt found. $(NH_4)_2SO_4$.	NH_4NO_3.
Mixed crystals of $(NH_4)_2SO_4$ and NH_4NO_3.	0·0243	0·1201	3·95	94·5
,, ,, ,,	0·0811	0·0870	17·34	80·91
,, ,, ,,	0·0898	0·0603	21·29	77·7
Na_2SO_4.	0·1046	0·2574	Na_2SO_4 93·9; $NaNO_3$ 2·4; $(NH_4)_2SO_4$ 0·72	
$NaNO_3$.	0·0501	0·2545	$NaNO_3$ 97·5	

In the mixed-crystal area, the proportion of ammonium sulphate separating increases steadily with increase of sulphate in the mixture. It is unfortunate that the complete ammonium nitrate–ammonium sulphate curve cannot be investigated.

The salt separating in the sodium sulphate area appeared to contain some nitrate, but the point representing the mixture taken was very near the border line between the sodium sulphate and sodium nitrate areas, so that a little nitrate was carried down with the sulphate.

All the experiments in this region were very difficult to perform.

Summary.

(1) A laboratory method of separating from the mother-liquor the crystalline deposits from fused salts has been worked out.

(2) The method has been applied with success to the reciprocal salt pairs: NH_4NO_3, NaCl; NH_4NO_3, KCl; NH_4NO_3, K_2SO_4; NH_4NO_3, Na_2SO_4.

(3) The results obtained confirm completely those derived from a consideration of the freezing-point curves.

UNIVERSITY COLLEGE, CARDIFF. [*Received, March 19th*, 1924.]

CLIII.—*Influence of Colloids on the Rate of Reactions Involving Gases. Part II. Decomposition of Hydrogen Peroxide and of Nitrosotriacetonamine.*

By ALEXANDER FINDLAY and WILLIAM THOMAS.

THE previous investigation (J., 1921, **119**, 170) of the influence of colloids on the rate of decomposition of hydroxylamine in presence of colloidal platinum was of a preliminary character. We now communicate the results of a more thorough investigation of the general problem, from which more definite conclusions can be drawn. Reactions are included in which gas is evolved, not only

from homogeneous, but also from heterogeneous systems, the reactions studied being (1) the decomposition of hydrogen peroxide by fuller's earth, (2) the decomposition of nitrosotriacetonamine in presence of hydroxide-ion, (3) the decomposition of hydrogen peroxide in presence of iodide-ion. The velocity of reaction was determined, as before, from the volume of gas evolved, and also, in the case of hydrogen peroxide catalysed by iodide-ion, by titration with permanganate.

In all cases, the reactions were carried out, at 27·5°, in a large boiling tube. The usual precautions with regard to the rate of stirring and the measurement of gas volumes were observed. The coefficient of reaction velocity was calculated in accordance with the expression for a unimolecular reaction, the minute being taken as the unit of time.

Colloids used.—The colloids, the influence of which was studied, were gelatin, starch, dextrin, albumin, and peptone; and care was taken, in each case, to prepare the colloidal sols in as uniform a manner as possible (see Findlay and King, J., 1913, **103**, 1170; 1914, **105**, 1297).

Experimental.

Reaction 1. *Decomposition of Hydrogen Peroxide in presence of Fuller's Earth.*—Merck's perhydrol, suitably diluted, was employed. In the absence of colloids, satisfactorily constant values were obtained for the velocity coefficient calculated for a unimolecular reaction from the volume of gas evolved from time to time, as was also shown by Rideal and Thomas (J., 1922, **121**, 2119). In presence of colloids, however, a different behaviour was found. If the colloidal sol was mixed with the hydrogen peroxide, and fuller's earth immediately added, decomposition of the hydrogen peroxide commenced at once and the rate of evolution of gas was relatively high, although always lower than when colloids were absent. The rate of evolution, however, diminished somewhat rapidly at first, and then more slowly, so that values were obtained for the velocity coefficient which rapidly fell but, in most cases, reached a fairly constant value. This variation of the value of the velocity coefficient for reactions carried out in colloidal media had previously been observed by Findlay and King (*loc. cit.*).

The fact that in our first series of experiments the velocity coefficient more or less quickly attained a fairly constant value led us to believe that the variation of the velocity coefficient during the reaction might be due to a change in the nature of the colloid, such as had been observed by Findlay and King. We therefore allowed fuller's earth and the colloidal sol to remain in contact for vary-

ing periods of time before adding them to the hydrogen peroxide, and we then found that the variation of the velocity coefficient became less as the period of contact increased up to 5 hours. The fact that even after prolonged contact variation of the velocity coefficient was still observed may find its explanation in an alteration of the colloid by the hydrogen peroxide. As we did not discover the influence of contact between the fuller's earth and the colloid until after we had concluded the whole series of measurements, we were able to investigate its effect only in the case of gelatin and of dextrin.

In Table I, the values of the velocity coefficient at 10, 100, and 300 minutes from the commencement of the reaction are shown, as read from our velocity coefficient–time curves. In the case of the gelatin and dextrin solutions, the A-values are those obtained when preliminary treatment of the fuller's earth with the colloid was not carried out, and the B-values are those obtained when the fuller's earth had been allowed to remain in contact with the colloid for 5 hours.

TABLE I.

Concentration of hydrogen peroxide: 0·0936 gm.-mol. per litre. Velocity coefficient of decomposition using 1 gram of fuller's earth per 100 c.c. of solution: $k = 0{\cdot}0953$.

Colloidal sol.		$k \times 10^4$. 10 mins.	100 mins.	300 mins.
Gelatin: 2·75%		294	145	105
,, 1·15%		361	285	256
,, 0·41%	A	853	524	417
	B	500	421	406
Starch: 2·00%		563	469	392
,, 1·32%		711	543	519
Dextrin: 1·98%		517	398	302
,, 0·85%	A	720	534	379
	B	581	469	372
Albumin: 0·85%		767	294	140
Peptone: 0·76%		627	449	217

The velocity coefficient after 300 minutes is approximately constant, except in the case of the reactions in presence of albumin and peptone, for which, especially for the latter, the velocity coefficient-time curves still show a distinct downward slope. In the case of the B solutions, the relatively constant value of the velocity coefficient agrees approximately with the value of k at 300 minutes.

By plotting the values of k at 300 minutes against concentration of colloid, it is found that the inhibitory effect of the colloids on the velocity of the reaction, as measured by the volume of gas evolved, is in the order albumin > peptone > gelatin > dextrin > starch. In the case of albumin and peptone, however, the influence of the colloid was studied only at one concentration. The behaviour of these two colloids, also, differed from that of the others, inasmuch as no

constant value for the velocity coefficient was reached at 300 minutes.

Reaction 2. *Decomposition of Nitrosotriacetonamine by Alkali.*—The decomposition of nitrosotriacetonamine by hydroxide-ion into phorone and nitrogen has been shown by Francis and Clibbens (J., 1912, **101**, 2358) and by Francis and Geake (J., 1913, **103**, 1722) to proceed according to the first-order equation, and the rate of decomposition is proportional to the concentration of hydroxide-ion.

Solutions of 0·015*N*-sodium hydroxide and of nitrosotriacetonamine were kept in the thermostat and mixed with water or with the solution of colloid in the reaction tube, and readings of the volume of gas evolved were begun as soon as possible thereafter. The amount of the nitroso-compound was such as to yield 40—50 c.c. of nitrogen. When the reaction took place in absence of colloids, the velocity coefficient calculated from the equation for a first-order reaction was found by us, as by Francis and Clibbens, to be practically constant and equal to 0·030. When, however, the nitrosotriacetonamine and alkali were added to the solution of a colloid, there was an initial fairly rapid fall in the value of the velocity coefficient, as in the decomposition of hydrogen peroxide with fuller's earth. This is seen from Table II, in which the values of the velocity coefficient at 5, 50, and 150 minutes are given.

TABLE II.

Colloidal sol.		$k \times 10^4$. 5 mins.	50 mins.	150 mins.
Gelatin :	1·97%	255	182	117
,,	1·01%	281	230	198
,,	0·58%	294	265	251
Starch :	2·05%	239	184	175
,,	0·96%	278	207	198
,,	0·42%	288	253	230
Dextrin :	1·05%	221	179	177
,,	0·54%	255	216	214
,,	0·21%	283	253	253
Albumin :	1·01%	242	185	177

Peptone has a specially powerful effect on the reaction. In presence of 0·41 per cent. of peptone, the reaction practically ceased, only 1 c.c. of gas being collected in 90 minutes.

The numbers in Table II show that k reaches a constant value more rapidly than in the case of the decomposition of hydrogen peroxide by fuller's earth. The fact that a constant value for k was reached pointed to an influence of the reactants on the colloid such as Findlay and King (*loc. cit.*) observed; and such an influence was readily proved. When, for example, the gelatin and alkali solutions were mixed together for some time before being added to

the nitrosotriacetonamine, the variation of the velocity coefficient was diminished, and after 3 hours' contact a constant velocity coefficient was obtained. In the case of the other colloids, a similar behaviour was found; the time of contact with alkali necessary in order to give a constant k-value, however, varied. A list of the k-values obtained after preliminary treatment of the colloid with alkali is given in Table III: a = time (hours) of contact with the alkali.

TABLE III.

		a.	$k \times 10^4$.			a.	$k \times 10^4$.
Gelatin:	1·97%	3	105	Dextrin:	1·65%	4½	152
,,	1·01%	,,	189	,,	0·54%	,,	209
,,	0·58%	,,	236	,,	0·21%	,,	244
Starch:	2·05%	12	111	Albumin:	1·01%	1	174
,,	0·96%	,,	170				
,,	0·42%	,,	216				

Reaction 3. *Decomposition of Hydrogen Peroxide with Iodide Ion as Catalyst.*—The investigation of this homogeneous reaction was undertaken, not only for the purpose of comparison with the decomposition of nitrosotriacetonamine, but also because it is a reaction the course of which can readily be followed by titration with permanganate as well as by means of the gas evolved. The importance of this fact for the purpose of our investigation will be discussed later.

The concentration of hydrogen peroxide was 0·0901 gm.-mol. per litre and that of the iodide 0·02167 gm.-mol. of potassium iodide per litre. The rate of reaction was again followed by measurement of the volume of gas evolved, and in the absence of colloids the velocity coefficient was found to be 0·0314. This value agrees well with that obtained by Bredig and Walton (*Z. physikal. Chem.*, 1904, **47**, 185).

In presence of colloids the behaviour of the system was analogous to that of the two systems previously described. That is to say, when the velocity of gas evolution was determined just after the hydrogen peroxide, iodide, and colloid had been mixed together, the velocity coefficient was found to have a relatively high value, higher, indeed (except in the case of peptone), than the value obtained in the absence of colloid. The velocity, however, rapidly decreased to a nearly constant value. In the case of peptone, a quite different behaviour was found; the value of the velocity coefficient rose fairly rapidly to a well-marked maximum and then fell off gradually and practically linearly with the time. No approach to a constant value was shown. The numbers given in Table IV indicate the course of the velocity coefficient–time curves.

When the 2·12 per cent. gelatin solution was left in contact with the iodide solution for some time before addition to the hydrogen

TABLE IV.

		$k \times 10^4$. 5 mins.	25 mins.	100 mins.
Gelatin :	2·12%	377	326	277
,,	0·95%	341	308	288
,,	0·10%	300	300	300
Starch :	2·92%	336	245	206
,,	1·25%	320	270	248
Dextrin :	2·94%	363	284	260
,,	1·33%	339	304	294
Albumin :	1·32%	405	319	298
Peptone :	0·79%	217	243 (max.)	180

peroxide, the values of $k \times 10^4$ at 5, 25, and 100 minutes were 298, 287, and 272, respectively.

The velocity of decomposition of hydrogen peroxide was also determined by titration with permanganate, the iodide being first precipitated by addition of a saturated solution of silver sulphate. Although the initial values were somewhat high, the mean values of the velocity coefficient were all, except in the case of peptone solutions, practically the same as that obtained in the absence of colloids. In the case of peptone solutions, no constant value for the velocity coefficient was obtained; the value remained fairly constant during the first half of the reaction and then fell off. The results obtained are shown in Table V.

TABLE V.

		$k \times 10^4$.		$k \times 10^4$.
Water		295	Starch : 1·18%	301—287
Gelatin :	1·95%	336—293	Dextrin : 1·50%	315—296
,,	0·98%	295	Peptone : 0·51%	232, then less.

Discussion.

As the result of our present investigation we are able to obtain a clearer understanding of the influence of colloids on the velocity of reactions involving gases than has hitherto been possible. We are able also to distinguish between the action of the two factors which *a priori* could be regarded as playing a part, namely, the influence of colloids on the chemical reaction itself and the influence of colloids on the rate of escape of gas from the reaction mixture.

Considering first the last reaction we studied, the decomposition of hydrogen peroxide in presence of iodide-ion, it is clear, from the numbers in Table V, that when the velocity of reaction is followed by titration with permanganate, the colloids gelatin, starch, and dextrin are practically without action on the rate of decomposition. This result is in conformity with that obtained by Reformatsky (*Z. physikal. Chem.*, 1891, **7**, 34), who found that the velocity of acid catalysis of methyl acetate in presence of agar-agar is unaffected

by the colloid. In the case of the decomposition of hydrogen peroxide, therefore, the fact that colloids lower the velocity coefficient of the reaction, when the velocity is determined from the volume of gas evolved, shows that it is the rate of formation of bubbles of gas in and of their escape from the reaction mixture that is being measured. In other words, in the case of a reaction which involves liberation of a gas and takes place in homogeneous solution, the velocity of the *chemical* reaction can be determined from the volume of gas evolved only when no colloids are present in the reaction mixture. In the presence of colloids, the volume of gas liberated in a given time is *not* a measure of the velocity of the chemical process.

Since, then, the colloid does not affect the velocity of the chemical reaction, it must influence the rate at which the gas escapes from the solution. This conclusion is, of course, not unexpected, because it has been shown by one of us in previous communications that the presence of colloids facilitates the occurrence of supersaturation in solutions of gases, and affects also the rate at which a gas escapes from supersaturated solution (Findlay and King, *loc. cit.*). These effects we may regard as being due, in large measure at least, to a "protective" action of the colloid on the minute bubbles of gas. Gas bubbles, as has been shown by McTaggart (*Phil. Mag.*, 1914, [vi], **27**, 297; **28**, 367), behave like colloidal particles. They are electrically charged and show adsorption effects like the colloidal particles of a solid. We may therefore assume that, owing to the adsorption of colloid, the growth of the minute gas bubbles is retarded.

When we consider the order of "protective" action, we find that the most effective of the colloids studied is peptone. The action of peptone also is peculiar, as is shown by the fact that the velocity coefficient of the reaction (measured by the gas evolved) increases to a maximum and then falls off, whereas in the case of the other colloids there is a rapid decrease in the velocity coefficient to a practically constant value. A similar abnormal behaviour of peptone was observed by Findlay and King (*loc. cit.*), in connexion with the escape of carbon dioxide from supersaturated solution. Even when the velocity coefficient is determined by titration, the abnormal influence of peptone is observed.

If, in comparing the influence of the other colloids on the velocity of reaction, as measured by the gas evolution, one considers the practically constant value of the coefficient reached after 100 minutes, it is found that starch has a much greater influence in reducing the velocity coefficient than gelatin, dextrin, or albumin. On plotting the values of the velocity coefficient against concentration of dextrin and gelatin, respectively, the curves are found to intersect

at a concentration of about 1·8 per cent., so that for percentages of colloid higher than this, dextrin lowers the velocity coefficient more than gelatin; whereas in more dilute solutions, gelatin is more effective than dextrin. The influence of albumin on the velocity coefficient is less than that of any of the other colloids.

A somewhat different result is obtained in the case of the decomposition of nitrosotriacetonamine in presence of alkali, a reaction which could be followed only by means of the gas evolved. On plotting the values recorded in Table III, it is found that the curves lie more closely together than in the preceding case. Moreover, the curve for gelatin cuts not only the curve for dextrin (at about 1·2 per cent. of colloid), as in the preceding case, but also the curve for starch, at a concentration of about 1·6 per cent. of colloid. At concentrations higher than 1·6 per cent. of colloid, gelatin has the greatest lowering effect on the velocity constant, and dextrin has the least; but at concentrations between 1·6 and 1·2 per cent. of colloid, the order is starch >gelatin >dextrin. At concentrations below 1·2 per cent., the order is starch >dextrin >gelatin. In other words, as compared with the hydrogen peroxide decomposition, the effects of gelatin and dextrin are reversed. The influence of albumin, in the concentration employed, is intermediate between those of starch and dextrin.

In the case of the decomposition of hydrogen peroxide by fuller's earth, we are dealing with a heterogeneous reaction analogous to the reaction we first studied, namely, the decomposition of hydroxylamine by platinum (*loc. cit.*), where the influence of added colloids was attributed to adsorption effects. The influence of colloids on this type of reaction has also been studied by Gróh (*Z. physikal. Chem.*, 1914, **88**, 414) and by Iredale (J., 1921, **119**, 109; 1922, **121**, 1536), who examined the inhibitory action of colloids on the catalytic decomposition of hydrogen peroxide by colloidal platinum. Both these investigators found that the effect of the added colloid could best be explained as due to adsorption. Iredale further found that the "inhibition numbers," or the minimum amounts of the colloids which affect the velocity of the reaction, run parallel with the Zsigmondy "gold numbers" of the colloids. Thus, in the case of the four colloids employed, Iredale found that the inhibitory influence is in the order gelatin >egg-albumin >dextrin >starch.

In the experiments which we have carried out with fuller's earth, it has to be borne in mind that the velocity coefficient was determined from the volume of gas evolved. The results obtained are therefore subject to the influence of two factors: (1) the inhibitory action of the colloids on the chemical reaction, as studied by Gróh and by Iredale, (2) the influence of colloids on the formation of gas

bubbles in, and their escape from, solution. If we assume, what, of course, is not necessarily the case, that the adsorption of the different colloids by fuller's earth runs parallel with the adsorption by colloidal platinum, then the order of the colloids as regards inhibitory action will be the same, so far as the chemical reaction is concerned, namely, gelatin >egg-albumin >dextrin >starch. On plotting the values of k at 300 minutes for the decomposition of hydrogen peroxide by fuller's earth, it is found that for this reaction also, when the rate of reaction is measured from the gas evolved, the inhibitory action of the colloids is in the order gelatin >dextrin > starch. The inhibitory action of albumin and of peptone is, however, much greater. On the other hand, if we assume that the influence of the colloids on the rate of escape of the gas is the same as in the decomposition of hydrogen peroxide by iodide-ion, for which the order of inhibitory effect is starch >dextrin >gelatin > albumin, or starch >gelatin >dextrin >albumin (according to the concentration of colloid), we see that, in the case of the heterogeneous reaction, the colloid acts mainly by reducing (by adsorption) the catalytic action of the solid catalyst.

Summary.

1. In a homogeneous system, the rate of a chemical reaction is not affected by the presence of colloids.

2. In a homogeneous system, the velocity coefficient of a reaction involving evolution of a gas can be determined from the volume of gas evolved only in the absence of colloids. When colloids are present, the velocity coefficient depends on the nature of the colloid and on its concentration.

3. When a reaction involving evolution of gas takes place under the influence of a solid catalyst, the rate of the chemical reaction as well as the rate of escape of gas is affected by the presence of colloids. The effect of the colloids on the chemical reaction appears to be greater than their effect on the rate of escape of gas.

UNIVERSITY OF ABERDEEN. [*Received, February 18th*, 1924.]

CLIV.—*Researches on Residual Affinity and Co-ordination. Part XVIII. Interactions of Zirconium Salts and β-Diketones.*

By GILBERT T. MORGAN and ARTHUR RILEY BOWEN.

THE earliest attempt to bring about chemical change between zirconium hydroxide or carbonate and acetylacetone in aqueous or alcoholic solution led to amorphous, ill-defined products (Mandl,

Z. anorg. Chem., 1903, **37**, 252), but in the following year Biltz and Clinch obtained decahydrated zirconium tetra-acetylacetone, $Zr(C_5H_7O_2)_4,10H_2O$, and converted this hydrate into anhydrous zirconium acetylacetone by repeated crystallisation from absolute alcohol (*ibid.*, 1904, **40**, 218). The existence of this tetra-acetylacetone derivative brings zirconium into line with its higher homologues of the fourth periodic group, namely, cerium and thorium, since these metals form similar compounds with acetylacetone.

By combining with four chelate acetylacetone groups, each of which functions as two associating units round the central metallic atom, the three metals manifest a similar co-ordination number of eight and in the case of zirconium this co-ordination index is confirmed by the composition of such inorganic compounds as the following: $ZrX_4,8NH_3$ (X = Cl, Br or I). Other inorganic derivatives of zirconium point, however, to a lower co-ordination number, namely, six, as indicated in the most stable type of zirconifluorides, R'_2ZrF_6, and this value is also displayed in the organic compounds $ZrCl_2(O{\cdot}C_6H_4{\cdot}CO_2Me)_2$ and $ZrCl_2(O{\cdot}C_6H_4{\cdot}COH)_2$, where the univalent radicals derived respectively from methyl salicylate and salicylaldehyde function as chelate groups. It is therefore evident that with zirconium the capacity for combining with associating units varies in different types of combination between the co-ordination values of six and eight.

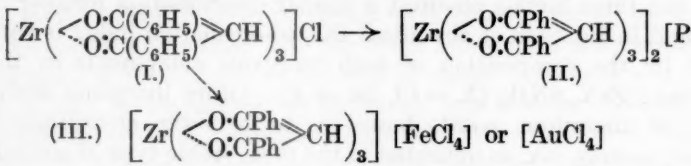
On attempting to combine the homologues of acetylacetone with zirconium nitrate in acidic aqueous solutions partly neutralised by sodium carbonate, the method adopted by Biltz and Clinch, it was not found possible to obtain definite crystalline products analogous with zirconium tetra-acetylacetone. Interaction with higher aliphatic diketones in aqueous solution was tried without success and double decomposition between sodium benzoylacetone and zirconium nitrate or oxychloride led to zirconyl bisbenzoylacetone, $[ZrO(C_{10}H_9O_2)_2]_3$.

Since these reactions in presence of water proved to be unpromising, experiments were then made with anhydrous zirconium tetrachloride and the β-diketones in dry media. In this way, a different mode of interaction was discovered which was shown to be general by applying it to the three typical cases of dibenzoylmethane, benzoylacetone, and acetylacetone. By operating in dry chloroform or benzene with zirconium tetrachloride and either of the foregoing β-diketones, three of the chlorine atoms of the tetrachloride are replaced by three chelate β-diketonic radicals, hydrogen chloride being evolved in accordance with the following general equation, where A$\bar{c}$ signifies the univalent diketonic chelate group:

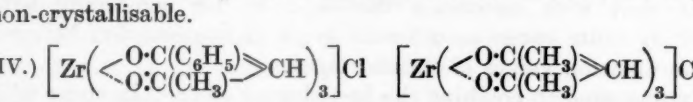
$$ZrCl_4 + 3HA\bar{c} = [ZrA\bar{c}_3]Cl + 3HCl.$$

Excess of the diketone and prolonged heating does not lead to complete substitution of diketonic radicals for the chlorine atoms, the compound formed in each case being zirconium tris-β-diketone chloride. It is, however, evident that the complexity of the β-diketone plays an important part in conducing to the stability of the product.

Zirconium trisdibenzoylmethane chloride (I), the most stable member of the series, can be preserved indefinitely in the dry state; it gives rise to crystallisable double salts such as the *ferrichloride* (III), *chloroaurate* (III), and *chloroplatinate* (II).



Zirconium trisbenzoylacetone chloride (IV) comes next in order of stability; its molecular weight corresponds with the graphic formula, and it gives rise to double chlorides with ferric chloride, auric chloride, and platinic chloride which, however, are oily and non-crystallisable.



Zirconium trisacetylacetone chloride (V) is the most readily hydrolysable of the series, but in the absence of moisture it is so stable that it may be crystallised unchanged from hot acetylacetone, thus showing that hydrolytic substitution of hydroxyl for the chlorine anion is an essential prelude to any change in the configuration of the co-ordination complex.

In the presence of water and sodium acetylacetone, however, this hydrolysis occurs and zirconium trisacetylacetone chloride is thus converted forthwith into the decahydrated zirconium tetra-acetylacetone.

When zirconium trisdibenzoylmethane chloride (I) is heated with excess of acetylacetone, the three aromatic diketonic residues are completely replaced by acetylacetone radicals and zirconium trisacetylacetone chloride (V) is obtained.

So long as these reactions are performed in anhydrous solvents the type of co-ordination complex remains unchanged and in these tris-β-diketonic derivatives zirconium displays a striking analogy with its lower homologues, titanium and silicon, the tetrachlorides of which elements have been shown by Dilthey to interact in a similar way with β-diketones in anhydrous solvents. With silicon

tetrachloride the general type is $[SiA\bar{c}_3]Cl$ and the analogy extends to the double chlorides, $[SiA\bar{c}_3]FeCl_4$, $[SiA\bar{c}_3]AuCl_4$, and $[SiA\bar{c}_3]_2PtCl_6$. So close is the similarity that analogous derivatives are found to contain the same solvent of crystallisation; $[Zr\ Dibenz_3]FeCl_4$ was found to crystallise with chloroform of crystallisation (compare $[Si\ Dibenz_3]AuCl_4,CHCl_3$, Dilthey, *Ber.*, 1903, **36**, 1598).

With titanium tetrachloride, the initial products with the diketone have the empirical general formula $TiA\bar{c}_2Cl_2$, but Dilthey showed that the substances are really trimeric $[TiA\bar{c}_3]_2TiCl_6$ by converting them into the double chlorides $[TiA\bar{c}_3]FeCl_4$, $[TiA\bar{c}_3]AuCl_4$, and $[TiA\bar{c}_3]_2PtCl_6$. This comparison shows that silicon and zirconium behave similarly in regard to the constitutions of the tris-β-diketone chlorides and of their double chlorides, and that as regards the latter series of salts this analogy may be extended to titanium.

Moreover, in its combinations with acetylacetone, zirconium shows its transitional position between the metals and non-metals of the fourth periodic group. In its capacity as metal it resembles cerium and thorium in yielding the tetra-acetylacetone derivative; as a metalloid it resembles titanium and silicon in giving rise to the trisacetylacetone type of combination.

Experimental.

I. *Interaction of Zirconium Tetrachloride and β-Diketones in Anhydrous Media.*

Preparation of Anhydrous Zirconium Tetrachloride.—The starting materials employed in the following experiments were Brazilian zirkite in the form of rock or pebbles ("favas") supplied by Messrs. Trost Bros., of Coventry, in two grades of 80 and 90 per cent. ZrO_2, and zirconia (97 per cent. ZrO_2, Messrs. Johnson and Matthey).

The finely powdered zirkite (passing through a 90-mesh sieve) was converted to the sulphate by evaporation with concentrated sulphuric acid and the impurities, ferric and titanium chlorides, were removed by crystallisation of the oxychloride, $ZrOCl_2,8H_2O$, from concentrated hydrochloric acid. The tartaric acid method of Dittrich and Pohl (*Z. anorg. Chem.*, 1905, **43**, 236) was also used as an alternative for the separation of iron.

Hevesy (*Chem. and Ind.*, 1923, **42**, 929) states that Brazilian zirkite contains approximately 1 per cent. of hafnium, and shows that hafnium ammonium fluoride and hafnium ammonium sulphate are more soluble than the corresponding zirconium double salts. Accordingly, a further purification of zirconium sulphate was effected by evaporating over sulphuric acid a solution containing 10 grams

of zirconium sulphate dissolved in 20 c.c. of water and 14 grams of ammonium sulphate (3 mols.) in 25 c.c. of water. The double zirconium ammonium sulphate, $(NH_4)_4[Zr_4(OH)_8(SO_4)_6],14H_2O$, crystallised out (Rosenheim and Pinsker, *Z. anorg. Chem.*, 1919, **106**, 10), and afforded also a ready separation from last traces of iron, which were converted into the more soluble ferric ammonium alum.

Anhydrous zirconium tetrachloride was prepared from purified zirconia by heating this dioxide in a stream of chlorine and carbon tetrachloride at 550—600°, the yield of tetrachloride being quantitative (Lely and Hamburger, *Z. anorg. Chem.*, 1914, **87**, 209; Venable and Bell, *J. Amer. Chem. Soc.*, 1917, **39**, 1598).

As the source of heat, a small electric furnace was used 18 inches in length and the zirconia was heated in a silica tube of 1 inch internal diameter, joined to a glass receiving tube 2 feet in length and 1¼ inches in internal diameter. These tubes were connected by a bung made of asbestos and waterglass, a glass-wool filter being attached to the outer end of the condenser. A stream of dry chlorine was bubbled through carbon tetrachloride and the mixed gas and vapour were carried over the heated zirconia. The zirconium tetrachloride thus obtained in pure white, lustrous crystals was quickly transferred to stoppered bottles, which were sealed with paraffin wax.

Zirconium Trisdibenzoylmethane Chloride (I).—Zirconium tetrachloride (2·6 grams; 1 mol.) was heated under reflux in 50 c.c. of chloroform B.P. with 7·3 grams of dibenzoylmethane (3 mols.) until the evolution of hydrogen chloride ceased. To the filtered solution light petroleum was added and the liquid left for a few hours in a stoppered bottle, when yellow, complex, pyramidal crystals separated, m. p. 258° (yield 7·3 grams or 82 per cent.). The product was stable in air, insoluble in ether or light petroleum, sparingly soluble in alcohol, acetone, benzene, toluene, or chloroform, dissolving readily in glacial acetic acid. It crystallised best from the last solvent or from chloroform, the melting point rising to 262°. Hydrolysis occurred when the acetic acid solutions were exposed to air. The condensation was also effected in dry benzene, when 0·9 gram of zirconium tetrachloride and 2·7 grams of dibenzoylmethane were refluxed in 75 c.c. of this solvent until hydrogen chloride was no longer evolved. The product was isolated by adding light petroleum and by concentrating the solution in a vacuum (yield 1·6 grams) [Found: C = 67·32, 67·42; H = 4·31, 4·38; Cl (grav.) = 4·38, 4·50; (vol.) 4·84, 4·50; Zr = 11·24, 11·17. $C_{45}H_{33}O_6ClZr$ requires C = 67·90; H = 4·15; Cl = 4·50; Zr = 11·20 per cent.].

Zirconium trisdibenzoylmethane chloride was also prepared by double decomposition between zirconium tetrachloride (2 mols.) and copper dibenzoylmethane (3 mols.) when 0·9 gram of the former reacted with 2·7 grams of the latter in 50 c.c. of chloroform B.P., the mixture being warmed for a few minutes on the water-bath and left for 2 hours at the ordinary temperature. Cupric chloride was removed and the filtrate concentrated in a vacuum (yield 82 per cent.). When heated in an ignition tube, zirconium trisdibenzoylmethane chloride decomposed, evolving hydrogen chloride and chlorodibenzoylmethane. Aqueous or alcoholic ferric chloride developed an immediate red coloration.

Zirconium Trisdibenzoylmethane Ferrichloride (III).—On adding 0·24 gram of anhydrous ferric chloride (1 mol.) to 1·72 grams of zirconium trisdibenzoylmethane chloride in 50 c.c. of chloroform B.P., a transient violet colour appeared and changed to yellow. The solution was heated under reflux, filtered, and diluted with light petroleum until an oil separated which subsequently crystallised in large, six-sided, orange-yellow prisms charring at 160° and melting at 163°. This preparation was soluble in warm alcohol, chloroform, or glacial acetic acid and dissolved in pyridine to a deep red solution. After a week in the desiccator the crystals became opalescent. When heated in an ignition tube, the product gave the odour of chloroform, and the presence of this substance was confirmed by applying the phenylcarbylamine reaction (Found : Zr = 8·83; Fe = 5·23; total oxides $ZrO_2 + Fe_2O_3$ = 19·42; Cl = 20·43, 20·75. $C_{45}H_{33}O_6ZrFeCl_4,\frac{2}{3}CHCl_3$ requires Zr = 8·74; Fe = 5·40; total oxides = 19·54; Cl = 20·54 per cent. A specimen heated for 3 hours at 90° lost 7·69. Theoretical loss for $\frac{2}{3}CHCl_3$ = 7·61 per cent.). A larger portion of the ferrichloride containing chloroform was heated at 90° until of constant weight and the residue was analysed [Found : Zr = 9·07; Fe = 6·07; total oxides = 20·95; Cl = 14·67 (Carius), 15·14 (hydrolysis). $C_{45}H_{33}O_6ZrFeCl_4$ requires Zr = 9·46; Fe = 5·83; total oxides = 21·15; Cl = 14·82 per cent.]. When crystallised from hot glacial acetic acid, the ferrichloride containing chloroform separated in well-defined, yellow, obliquely truncated prisms charring at 110°.

Zirconium Trisdibenzoylmethane Chloroaurate (III).—A chloroform solution (35 c.c.) of 0·128 gram of auric chloride hydrochloride, $AuCl_3,2HCl$ (Johnson and Matthey) and 0·2684 gram of zirconium trisdibenzoylmethane chloride was heated for a few minutes under reflux, concentrated in a vacuum, and treated with light petroleum. An oil separated which gradually solidified to a yellow, crystalline powder. This chloroaurate charred at 150° and melted at 155—156°; it was slightly soluble in cold chloroform, warm alcohol,

acetone, or benzene. It dissolved with decomposition in hot glacial acetic acid, colloidal gold being set free; it was insoluble in ether or light petroleum (Found: Au = 17·96; Zr = 7·92; Au + ZrO_2 = 28·68; Cl = 13·27. $C_{45}H_{33}O_6ZrAuCl_4$ requires Au = 17·94; Zr = 8·24; Au + ZrO_2 = 29·10; Cl = 12·92 per cent.).

Zirconium Trisdibenzoylmethane Chloroplatinate (II).—A molecular proportion (0·1676 gram) of anhydrous chloroplatinic acid, H_2PtCl_6 (Johnson and Matthey), dissolved in a small quantity of glacial acetic acid, was added to 0·6510 gram (2 mols.) of zirconium trisdibenzoylmethane chloride in 30 c.c. of glacial acetic acid, when a pulverulent, orange-yellow, crystalline double salt separated. It charred and decomposed at 210—220° and was insoluble in water and organic media [Found: Pt = 10·09; Zr = 9·66; ZrO_2 + Pt = 23·17; Cl = 11·45, 11·61. $(C_{45}H_{33}O_6Zr)_2PtCl_6$ requires Pt = 10·13; Zr = 9·40; ZrO_2 + Pt = 22·85; Cl = 11·05 per cent.].

Zirconium Trisbenzoylacetone Chloride (IV).—Zirconium tetrachloride (3·1 grams; 1 mol.) and 4·5 grams of benzoylacetone (3 mols.) in 50 c.c. of anhydrous benzene were heated under reflux for 2 hours; the solution was then filtered and concentrated in a vacuum, when pale yellow, rhomboidal prisms separated. Recrystallised from benzene, the product melted at 124—125°; it was soluble in alcohol, benzene, chloroform, or glacial acetic acid and was precipitated from these solvents on the addition of light petroleum. From benzene and petroleum, it crystallised in clusters of prisms, m. p. 126—127° (Found: C = 59·47; H = 4·61; Cl = 5·81, 5·89; Zr = 14·47; M = 614, cryoscopic method in benzene. $C_{30}H_{27}O_6ClZr$ requires C = 59·11; H = 4·43; Cl = 5·83; Zr = 14·55 per cent.; M = 609·1).

Zirconium trisbenzoylacetone chloride developed immediately a red coloration with aqueous ferric chloride; it was stable in the desiccator, but hydrolysed by moist air. An alcoholic solution of the tris-diketone chloride and silver nitrate gave an immediate precipitate of silver chloride.

Attempts were made to prepare double chlorides by warming this chloride with chloroplatinic acid, chloroauric acid, or ferric chloride in well-dried benzene, chloroform, or glacial acetic acid, but in each case the addition of light petroleum led to the separation of oily products.

Zirconium Trisacetylacetone Chloride (V).—Zirconium tetrachloride (2·5 grams; 1 mol.) and 4·5 grams of acetylacetone (4 + mols.) were heated under reflux with 30 c.c. of purified anhydrous chloroform until evolution of hydrogen chloride had ceased. The filtered solution on concentration in a vacuum desiccator yielded large, transparent, colourless prisms, which were hydrolysed by moist

air, liberating hydrogen chloride and acetylacetone. The compound was soluble in water (with decomposition) and in alcohol, chloroform, acetone, glacial acetic acid, or warm benzene, but insoluble in ether or petroleum; an alcoholic solution developed a red coloration with aqueous ferric chloride. An alcoholic solution added to alcoholic silver nitrate gave an instant precipitate of silver chloride.

Zirconium trisacetylacetone chloride separated from dry benzene in colourless crystals and was recrystallised without change from warm acetylacetone, when well-defined, colourless prisms were obtained, m. p. 101—102° (Found: C = 41·93; H = 5·12; Cl = 8·31, 8·36; Zr = 21·30, 21·36; M = 418, ebullioscopic method in benzene. $C_{15}H_{21}O_6ClZr$ requires C = 42·55; H = 4·96; Cl = 8·38; Zr = 21·40 per cent.; M = 423).

Zirconium trisacetylacetone chloride was also prepared by double decomposition from zirconium tetrachloride (2 mols.) and copper acetylacetone (3 mols.) in dry benzene, but owing to sparing solubility in this solvent it had to be extracted with hot benzene from the by-product, cupric chloride.

Although zirconium trisacetylacetone chloride separated unchanged from warm dry acetylacetone, it was converted into decahydrated zirconium tetra-acetylacetone under the following conditions: 1·30 grams of $[ZrA\bar{c}_3]Cl$ were dissolved in 19·5 c.c. of water, 0·32 gram of acetylacetone was added with sufficient aqueous sodium carbonate to dissolve it, the solution remaining faintly acid; 0·7 gram of zirconium tetra-acetylacetone was obtained in the first crop of crystals [Found: Zr = 13·35. $Zr(C_5H_7O_2)_4,10H_2O$ requires Zr = 13·56 per cent.].

The decahydrated zirconium tetra-acetylacetone obtained in the preceding experiment and a similar specimen prepared by Biltz and Clinch's method from zirconium nitrate were recrystallised twice from acetylacetone. Both preparations were rendered anhydrous by this procedure; they melted at 193—195° and did not depress each other's melting points. The specimen prepared from zirconium trisacetylacetone chloride was analysed [Found: Zr = 18·51. $Zr(C_5H_7O_2)_4$ requires Zr = 18·62 per cent.].

Interconversion of Zirconium Tris-β-diketone Chlorides.—When zirconium trisdibenzoylmethane chloride was crystallised from the minimum quantity of acetylacetone, the product precipitated by light petroleum consisted of unchanged dibenzoylmethane derivative, a certain amount of zirconium trisacetylacetone chloride, and mixed crystals of the two salts. With excess of acetylacetone, the conversion was complete, and the product deposited by light petroleum consisted entirely of colourless, prismatic needles of *zir-*

conium trisacetylacetone chloride [Found : Cl = 8·29. $Zr(C_5H_7O_2)_3Cl$ requires Cl = 8·38 per cent.].

II. *Interaction of Zirconium Salts and β-Diketones in Aqueous Solution.*

Zirconium tetra-acetylacetone, $ZrA\bar{c}_4,10H_2O$, prepared from zirconium nitrate by Biltz and Clinch's method, was obtained in similar yield and gave Zr = 13·42, 13·49, theory requiring Zr = 13·56 per cent.; it was dehydrated completely by five crystallisations from alcohol or preferably by two crystallisations from acetylacetone.

Experiments were then made with varying concentrations of zirconium nitrate and alkali and with the following homologues of acetylacetone: 3-methylacetylacetone, propionylacetone, and *n*-butyrylacetone, but in no case was a crystalline analogue of zirconium tetra-acetylacetone produced.

Benzoylacetone being less readily soluble in alkali than acetylacetone, the procedure was modified in this instance by using sodium benzoylacetone. Aqueous solutions of zirconium nitrate and sodium benzoylacetone in various concentrations gave a white precipitate, deposited from the faintly acid solution. The product was more conveniently prepared by interaction with zirconium oxychloride, $ZrOCl_2,8H_2O$.

Zirconyl Bisbenzoylacetone.—To a solution of 3·6 grams of oxychloride in 100 c.c. of water, 4·2 grams of sodium benzoylacetone in 100 c.c. of water were slowly added with stirring. A white, granular precipitate was slowly deposited (1·4 grams) which was soluble in alcohol, benzene, or glacial acetic acid. A specimen deposited from benzene solution on addition of light petroleum melted at 194° [Found : Zr = 21·34, 21·21. $(C_{10}H_9O_2)_2ZrO$ requires Zr = 21·14 per cent.]. Molecular-weight determinations in boiling benzene, although difficult owing to sparing solubility, indicated threefold association. $M = 1213$; theory requires $M = 1284$.

Note on the Analysis of Zirconium Tris-β-diketone Chlorides.

The foregoing zirconium compounds were readily hydrolysed by boiling aqueous potassium hydroxide, the chlorine-ion being estimated both gravimetrically and volumetrically in the filtrate from precipitated zirconium hydroxide, but in the exceptionally stable dibenzoylmethane derivative chlorine was estimated by the Carius method. Although zirconium trisacetylacetone chloride was a comparatively unstable, easily hydrolysed salt, it gave persistently low results in the carbon estimation until ignited copper oxide was mixed with the weighed substance in order to oxidise traces of carbon probably retained in the form of zirconium carbide.

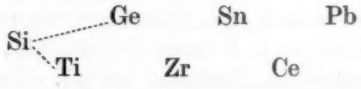
The authors desire to express their thanks to the Government Grant Committee of the Royal Society and to the Advisory Council of the Department of Scientific and Industrial Research for grants which have helped to defray the expense of this investigation.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON. [*Received, March 11th*, 1924.]

CLV.—*Researches on Residual Affinity and Co-ordination. Part XIX. Interactions of Germanium Tetrahalides and β-Diketones.*

By GILBERT T. MORGAN and HARRY DUGALD KEITH DREW.

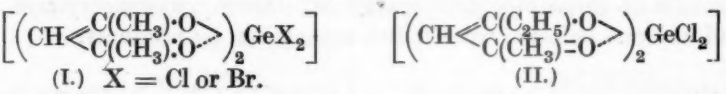
THE elements of the fourth vertical series of the conventional periodic classification are divisible into two well-defined natural families which, excluding the initial element, carbon, may be regarded as branching off from silicon.



The upper series including silicon is distinguished from the lower by the property possessed by all its members of forming organic derivatives. This capacity for combination with organic radicals has so far not been observed in the titanium family. In other respects, there are many points of similarity between these two related families.

With the exception of germanium, the members of both families have yielded characteristic compounds with acetylacetone and other β-diketones, these products indicating a gradation in the tendency to form co-ordination compounds which is noticeable as the atomic weight increases. The present communication deals with the interactions of the germanium tetrahalides and acetylacetone either free or in the form of its copper derivative.

Germanium tetrachloride reacts energetically with acetylacetone in anhydrous solvents, hydrogen chloride is evolved, and *germanium bisacetylacetone dichloride* (I) is produced in quantitative yield.



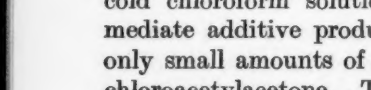
The reaction with germanium tetrabromide is much more sluggish, very little hydrogen bromide is liberated, and the yield of *germanium bisacetylacetone dibromide* (I) is correspondingly small. Possibly

this change is incomplete on account of the stability of germanibromic acid, H_2GeBr_6, as compared with the corresponding chloro-compound, which readily dissociates evolving hydrogen chloride, and these differences are reminiscent of the interaction of acetylacetone and the tin tetrahalides (this vol., p. 373).

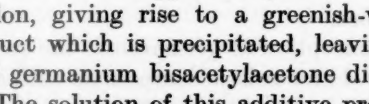
Although the dichloride gave indications of having the monomeric formula, the germanium bisacetylacetone dihalides (I) are somewhat sparingly soluble in organic media suitable for molecular-weight determinations, and accordingly the molecular complexity of this type of β-diketonic derivative was ascertained with greater certainty by preparing the more soluble *germanium bispropionylacetone dichloride* (II) from the tetrachloride and propionylacetone. Molecular-weight determinations by ebullioscopic and cryoscopic methods gave numbers corresponding with the monomeric structure, which is accordingly adopted for all three diketonic derivatives.

In the interactions between the free β-diketone and its tetrahalides, germanium has behaved so far in a precisely similar manner to tin, for in the case of both metals only half the halogen is replaced by the chelate diketone radical and, moreover, the resulting products have the general monomeric formula $[R{\cdot}A\bar{c}_2hal_2]$, where R is the metal and $A\bar{c}$ the univalent diketonic radical. Tin, however, gave the same type of acetylacetone derivative even when the diketone was employed in the form of its copper salt. But with germanium this mode of interaction led to further replacement of halogen by acetylacetone radicals.

Germanium tetrachloride and copper acetylacetone interact in cold chloroform solution, giving rise to a greenish-white, intermediate additive product which is precipitated, leaving dissolved only small amounts of germanium bisacetylacetone dichloride and chloroacetylacetone. The solution of this additive product in hot acetylacetone deposited on cooling a complex mixture of blue, orange-yellow, and colourless crystals. The blue products, which contained bivalent copper, were very unstable when dissolved in cold chloroform and changed into colourless *germanium trisacetylacetone cuprochloride* (III). The yellow product in contact with acetylacetone even in the cold slowly underwent a similar decomposition into the colourless cuprochloride (III). In the decomposition of these blue and orange substances, chloroacetylacetone and cuprous chloride were found among the by-products.



(III.) $X_2 = Cl_2$ or Br_2.



(IV.)

The interaction between germanium tetrabromide and copper

acetylacetone in chloroform gives rise to purple-black products containing bivalent copper, which are probably germanium tris-acetylacetone cupribromides. These intensely coloured compounds are, however, very unstable in all organic media which dissolve them; they become decolorised and finally yield colourless *germanium trisacetylacetone cuprobromide* (III) and *germanium trisacetylacetone dicuprobromide* (IV), which are comparatively stable substances unchanged by exposure under atmospheric conditions.

The complex cuprochloride and cuprobromides contain respectively germanium trisacetylacetone chloride and bromide, $[GeA\bar{c}_3]X$, which have not yet been definitely isolated. The radical $GeA\bar{c}_3$ of the co-ordination complex simulates the behaviour of the alkali metals or ammonium, as is shown by a comparison of the following series:—(i) $KCuCl_2$ and $[GeA\bar{c}_3]CuCl_2$; (ii) NH_4CuBr_2 and $NH_4Cu_2Br_3$; $[GeA\bar{c}_3]CuBr_2$ and $[Ge\ A\bar{c}_3]\ Cu_2Br_3$.

The presence of the radical $GeA\bar{c}_3$ in the germanium series shows that this element resembles silicon and titanium, although the conditions under which the three acetylacetone groups are introduced into the co-ordination complex are somewhat different. Silicon and titanium tetrachlorides react with the free β-diketone and the formation of tris-β-diketonic derivatives represents the sole mode of action, whereas with germanium tetrachloride the free diketone replaces only two chlorine atoms by the acetylacetone radical and the employment of copper acetylacetone becomes necessary in order to displace the third halogen atom. So far it has not been found possible to replace the fourth chlorine by an acetylacetone group.

In this respect, it is interesting to compare germanium and zirconium. When treated with acetylacetone, zirconium salts in aqueous media give rise to zirconium tetra-acetylacetone, but by operating in anhydrous solvents it has recently been found that both the free diketones and their copper derivatives replace only three of the chlorines of zirconium tetrachloride. The products have the general type formula $ZrA\bar{c}_3Cl$, and, in the case of the dibenzoylmethane derivative, give rise to complex salts of the type $[ZrA\bar{c}_3]AuCl_4$.

The various modes of interaction with acetylacetone and its copper derivatives exhibited by elements in the fourth periodic series are shown in the following diagram:

$[SiA\bar{c}_3]AuCl_4$.	$[GeA\bar{c}_3]CuX_2$		
	$[GeA\bar{c}_2X_2]$	$[SnA\bar{c}_2X_2]$	$PbA\bar{c}_2$.
$[TiA\bar{c}_3]FeCl_4$	$[ZrA\bar{c}_3]Cl$.	$CeA\bar{c}_3$	
	$ZrA\bar{c}_4$	$CeA\bar{c}_4$	$ThA\bar{c}_4$.

The results described in the present communication have completed this comparative study by extending the survey to the case of germanium.

Experimental.

Germanium, obtained as a heavy, greyish-black powder, was produced by heating pure germanium dioxide (Foote Mineral Co., U.S.A.) in a current of hydrogen (Winkler, *J. pr. chem.*, 1887, [ii], **36**, 177; Dennis and Hance, *J. Amer. Chem. Soc.*, 1922, **44**, 299).

Germanium tetrabromide was prepared in quantitative yield by adding a slight excess of bromine to germanium contained in a distillation apparatus protected from atmospheric moisture. Bromination proceeded without external heating, until the metal was completely attacked, when the product was distilled. The trace of bromine remaining in the germanium tetrabromide was removed by leaving this compound in a flask with an indiarubber stopper, when the halogen was absorbed by the rubber, leaving the tetrabromide as a colourless, ice-like solid (b. p. 180—182°/740 mm.). Mercury is unsuitable for removing any very appreciable amount of bromine, since the tetrabromide becomes contaminated with the complex salt, $HgGeBr_6$.

Germanium tetrachloride was obtained in quantitative yield by successively heating and cooling the metal in a slow current of dry chlorine, nitrogen being subsequently passed through the tetrachloride to free it from dissolved chlorine (Dennis and Hance, *loc. cit.*).

I. *Interaction of Germanium Tetrahalides and Acetylacetone.*

Germanium bisacetylacetone dichloride (formula I), prepared by digesting for 1½ hours on the water-bath 1·6 grams of germanium tetrachloride, 3·2 grams of acetylacetone (4 mols. +) and 25 c.c. of pure chloroform, separated from the clear, colourless solution on cooling in colourless crystals (yield 76 per cent.). It was recrystallised from a mixture of chloroform and acetylacetone in small, colourless prisms becoming yellow at 236° and melting with intumescence at 240°. This dichloride, which was very sparingly soluble in the majority of organic media, was decomposed by hydroxylic solvents (Found: C = 34·91; H = 4·23; Cl = 20·82; Ge = 20·53. $C_{10}H_{14}O_4Cl_2Ge$ requires C = 35·16; H = 4·13; Cl = 20·77; Ge = 21·20 per cent.). The dichloride dissolved slowly in pure chloroform (Boots') and a molecular-weight determination by the ebullioscopic method in this solvent ($c = 0·405$) gave $M = 341$, theoretical value $M = 341·5$.

Germanium Bisacetylacetone Dibromide (Formula I).—After heating under reflux for 2½ hours, 5·2 grams of germanium tetrabromide

and 5·3 grams of acetylacetone in 25 c.c. of dry chloroform B.P., the solution became pale yellow, but no evolution of hydrogen bromide was apparent. The solvent was then removed by distillation and the residual liquid, which contained a large excess of acetylacetone, was boiled for 30 minutes. The dark brown oil, from which no appreciable amount of hydrogen bromide had been evolved, was freed from acetylacetone in a vacuum desiccator, when it partly solidified, the total amount of crystals being 1·1 grams. An even smaller yield (0·2 gram) was obtained from 3·2 grams of tetrabromide and 3·3 grams of acetylacetone heated in 15 c.c. of dry benzene for 2 hours. *Germanium bisacetylacetone dibromide* was a colourless, microcrystalline powder very insoluble in the volatile organic solvents, but dissolving in boiling acetylacetone. Decomposition set in on prolonged boiling, and the substance was also decomposed by hot alcohol or by cold water, in the last case the products being germanium dioxide, hydrogen bromide, and acetylacetone. It melted at 226° with intumescence (Found: C = 27·26, 27·28, 27·26; H = 3·47, 3·84, 3·54; Br = 37·15; Ge = 16·77. $C_{10}H_{14}O_4Br_2Ge$ requires C = 27·89; H = 3·28; Br = 37·14; Ge = 16·82 per cent.). In these compounds, germanium was estimated by slow evaporation with dilute nitric acid and then with stronger acid, the germanium dioxide being finally ignited in a porcelain crucible surrounded by a silica one.

II. *Germanium Bispropionylacetone Dichloride* (Formula II).

To 4·5 grams of germanium tetrachloride in 50 c.c. of pure chloroform were added 9·6 grams (4 mols.) of propionylacetone. A slight rise of temperature occurred, and the liquid became turbid, but cleared on heating under reflux, when hydrogen chloride was evolved. After 4 hours, additional 5 grams of propionylacetone were introduced and the heating was continued for the same time. The solvent was removed by distillation and the residual oil concentrated slowly in a vacuum, when a white, crystalline precipitate separated and was washed with carbon tetrachloride to remove the oily mother-liquor (yield 80 per cent.). The product, although more soluble, was less stable than the two preceding compounds and deteriorated when crystallised from hot organic solvents. However, when dissolved in cold chloroform, the solution yielded on adding light petroleum a white, crystalline powder melting at 128—129° to a transparent, colourless liquid (Found: Ge = 19·57; Cl = 19·10. $C_{12}H_{18}O_4Cl_2Ge$ requires Ge = 19·59; Cl = 19·19 per cent.). Ebullioscopic determinations of molecular weight gave 321 (in chloroform) and 479, 470 (in benzene), whereas cryoscopic estimations in the latter solvent gave 378, 381. $Ge(C_6H_9O_2)_2Cl_2$ requires

$M = 370$. The latter data are the more trustworthy, since from boiling solvents the substance was recovered with lowered melting point.

III. *Germanium Tetrachloride and Copper Acetylacetone.*

Germanium tetrachloride reacts towards copper acetylacetone dissolved in chloroform quite differently from the tetrabromide (*v. infra*), for in the present case the bulk of the germanium is precipitated in an insoluble green powder which contains combined copper salts. The proportions studied were $2GeCl_4 : 3CuA\bar{c}_2$ (1·9 grams of tetrachloride and 3·4 grams of copper derivative in 25 c.c. of chloroform) and $1GeCl_4 : 2CuA\bar{c}_2$ (2·7 grams of tetrachloride and 6·4 grams of copper salt in 30 c.c. of chloroform). After 24 hours in the cold, the blue solution had become colourless with a greenish-white precipitate (4·2 and 8·0 grams, respectively). The mother-liquor on evaporation furnished germanium bisacetylacetone dichloride (0·9 and 0·5 gram) and a small amount of chloroacetylacetone.

When boiled with acetylacetone, the greenish-white precipitate disssolved to an olive-brown solution, leaving a residue of cuprous chloride. On cooling, the filtrate deposited successively (i) colourless germanium bisacetylacetone dichloride, (ii) well-defined, dark blue needles melting and decomposing at temperatures ranging from 130° to 160°, (iii) a green powder decomposed by aqueous chloroform into cupric chloride and copper acetylacetone, (iv) transparent, six-sided, bright orange to yellow crystals, m. p. 129°, (v) colourless prisms, m. p. 145°. The final mother-liquor contained chloroacetylacetone.

ii. *The blue compounds.*—On one occasion, a small amount of dark blue needles was obtained decomposing at 161—162°. However, the blue product generally obtained melted at 137—139° [Found: C = 30·16, 29·33; H = 3·49, 3·55; Cl = 20·25, 20·86. These data correspond with the complex formula $Ge_2(C_5H_7O_2)_6Cl_7Cu_3$, for which C = 30·57; H = 3·59; Cl = 21·07 per cent.].

In cold chloroform the blue substance changed appreciably, dissolving partly, and leaving a residue of cupric and cuprous chlorides; the solution yielded on concentration colourless, four-sided prisms with pyramidal ends of *germanium trisacetylacetone cuprochloride* (m. p. 147—148°) and a small proportion of the orange-yellow compound (m. p. 129°) separating in compact prisms.

iv. *The orange-yellow compound* (m. p. 128—129°) separated from acetylacetone in compact, transparent, orange-yellow, highly refractive prisms and from chloroform in efflorescent crystals breaking down to a primrose-yellow powder. It was only sparingly soluble in the

ordinary organic media, but dissolved more freely in warm acetylacetone, although prolonged contact with this solvent led to decomposition into germanium trisacetylacetone cuprochloride, chloroacetylacetone, small amounts of cuprous chloride and a fusible product (m. p. 80°) containing germanium. Water or aqueous caustic soda hydrolysed the compound (Found : C = 35·97, 36·45; H = 4·50, 4·46; Cl = 15·31, 15·20. $(C_5H_7O_2)_7Cl_5Cu_2Ge_2$ requires C = 36·77; H = 4·32; Cl = 15·51 per cent.).

v. *Germanium trisacetylacetone cuprochloride* (formula III) separated in transparent, colourless, refractive, acicular prisms of square section and with pyramidal ends; it melted at 147—148° to a transparent, red liquid (Found : Cl = 13·76. $C_{15}H_{21}O_6Cl_2CuGe$ requires Cl = 14·07 per cent.). It was readily soluble in chloroform and was decomposed by cold aqueous caustic alkali, yielding cuprous hydroxide.

IV. *Germanium Tetrabromide and Copper Acetylacetone.*

The following two proportions of reagents were studied in detail : (1) 3 Mols. $GeBr_4$: 4 mols. $Cu(C_5H_7O_2)_2$; to 6·5 grams of crystalline tetrabromide in 25 c.c. of chloroform were added 5·8 grams of copper acetylacetone in 60 c.c. of the same solvent, giving a blue solution containing a black precipitate changing to green. This deposit on treatment with boiling acetylacetone left cuprous bromide (2 grams) and the solution on concentration yielded a small amount of germanium trisacetylacetone dicuprobromide. The blue solution, which slowly became apple-green, was concentrated to 30 c.c., when a heavy oil and a purple precipitate were obtained. The latter was almost completely soluble in chloroform, leaving 1·1 grams of germanium bisacetylacetone dibromide (m. p. 212—214°). The chloroform solutions were again concentrated, when purple-black crystals (4·5 grams) separated melting at 137—139°. The admixed oil was removed by benzene and identified as bromoacetylacetone (3 grams).

(2) One mol. $GeBr_4$: 2 mols. $Cu(C_5H_7O_2)_2$; to 9·5 grams of tetrabromide in 60 c.c of chloroform were added 12·6 grams of copper acetylacetone in 100 c.c. of the same solvent. After 9 hours, 4·7 grams of cuprous bromide separated contaminated with germanium trisacetylacetone cuprobromide and dicuprobromide, which were extracted with hot acetylacetone. The green chloroform solution yielded only 0·2 gram of germanium bisacetylacetone dibromide and on concentration gave, as before, bromoacetylacetone and the purple-black substance (12·9 grams). This product had the chemical reactions of a mixture of germanium trisacetylacetone cupribromide and dicupribromide, the former compound predomin-

ating. This supposition was confirmed by titrating the coloured mixed cupribromides (10 parts) with copper acetylacetone (1 part) in chloroform solution. Cuprous bromide was precipitated and the decolorised solution, when evaporated to dryness in a desiccator, yielded bromoacetylacetone and a colourless, crystalline residue of germanium trisacetylacetone cuprobromide mixed with a small proportion of the corresponding dicuprobromide.

Germanium trisacetylacetone cuprobromide (formula III) dissolved readily in cold chloroform without decomposition and was thus separated from the dicuprobromide. On recrystallisation from hot acetylacetone, it separated in hard, colourless, transparent, rectangular prisms, sometimes having domed ends; it melted at 165—166° to a transparent, red liquid (Found: C = 30·05; H = 4·06; Br = 26·86; $GeO_2 + CuO$ = 30·46. $C_{15}H_{21}O_6Br_2CuGe$ requires C = 30·36; H = 3·57; Br = 26·95; $GeO_2 + CuO$ = 31·02 per cent.). This cuprobromide was quite stable in the air; it was unaffected by copper acetylacetone or by boiling chloroform, and gave no red coloration with ferric chloride in moist alcoholic chloroform. Aqueous caustic potash at once set free cuprous hydroxide. A molecular-weight determination in boiling chloroform ($c = 2$) gave a remarkably low elevation of boiling point (0·006—0·007°), indicating an extremely high association factor (more than twelvefold) corresponding with the high association exhibited by other salts in the same solvent (W. E. S. Turner, "*Molecular Association*," 1915, p. 31 and 34).

Germanium trisacetylacetone dicuprobromide (formula IV) remained insoluble when the preceding compound was dissolved in chloroform; it was, however, dissolved in hot acetylacetone and separated, on cooling the filtered solution, in colourless prisms or flakes melting at 195° to a brown, tarry liquid (Found: C = 24·47; H = 2·78; Br = 32·29; $GeO_2 + CuO$ = 36·18. $C_{15}H_{21}O_6Br_3Cu_2Ge$ requires C = 24·45; H = 2·87; Br = 32·55; $GeO_2 + CuO$ = 35·78 per cent.).

The acetylacetone mother-liquors from this dicuprobromide also contained its dissociation products cuprous bromide and the cuprobromide. Accordingly the dicuprobromide was also obtained synthetically by adding cuprous bromide to an acetylacetone solution of the cuprobromide.

Germanium Trisacetylacetone Cupribromide.—Although the purple-black product from germanium tetrabromide and copper acetylacetone probably contains at least two cupribromides, which have not yet been completely separated from one another, nevertheless one constituent has been synthesised by adding 0·135 gram of bromine (1 atom) in 10 c.c. of chloroform to 1 gram of germanium

trisacetylacetone cuprobromide (1 mol.) dissolved in 15 c.c. of this solvent. The intensely green solution on concentration in a desiccator left a green oil which solidified to a greenish-black, crystalline mass, m. p. 139°. This substance had an olive-green streak and with aqueous caustic potash it gave a yellowish-orange precipitate which blackened on boiling (Found : C = 26·29; H = 3·14; Br = 36·85; $GeO_2 + CuO$ = 26·39. $C_{15}H_{21}O_6Br_3CuGe$ requires C = 26·76; H = 3·15; Br = 35·63; $GeO_2 + CuO$ = 27·34 per cent.).

The authors desire to express their thanks to Messrs. Brunner Mond and Co., Ltd., for a grant which has partly defrayed the expense of this investigation.

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CLVI. *Action of Selenium Tetrachloride on Di- and Tri-ketones. Selenium Phenylacetyl- and β-Phenylpropionyl-acetones.*

By GILBERT T. MORGAN and CHARLES RAYMOND PORTER.

THE condensation of selenium tetrachloride and β-diketones has been extended, in the experiments described below, to certain complex di- and tri-ketones with the object of ascertaining to what extent the reaction noticed with the simpler diketones is a general one (compare J., 1922, **121**, 2432).

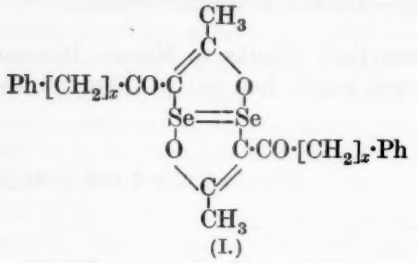
I. *Selenium Tetrachloride and β-Diketones,* $Ph{\cdot}[CH_2]_x{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3$.

ω-Phenylacetylacetone was selected in the first place because so far it has not given a definite result with tellurium tetrachloride. The copper derivative of this diketone when condensed with selenium tetrachloride reacts, however, smoothly to yield as main product the dimeric *selenium ω-phenylacetylacetone* (formula I or Ia, where $x = 1$), the other organic product being *3-chloro-ω-phenylacetylacetone* in accordance with the following equation :

$$2(C_{11}H_{11}O_2)_2Cu + 2SeCl_4 = (C_{11}H_{10}O_2)_2Se_2 + 2C_{11}H_{11}O_2Cl + 2CuCl_2 + 2HCl.$$

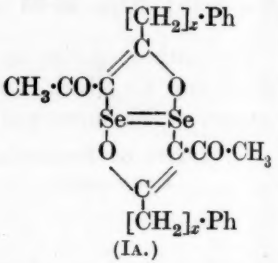
The course of the reaction resembles that observed in the case of acetylacetone, but differs in certain important details from the more complicated series of changes formerly elucidated in the condensations with benzoylacetone and dibenzoylmethane (*ibid.*, p. 2438 *et seq.*).

This resemblance to the purely aliphatic diketone is maintained in the second condensation described below, where β-*phenylpropionylacetone* is employed, this mixed diketone being also chosen because of the difficulty experienced in condensing it with tellurium tetrachloride. Its copper derivative, however, reacts readily with selenium tetrachloride, giving rise to the dimeric *selenium* β-*phenylpropionylacetone* (formula I or IA, where $x = 2$).*



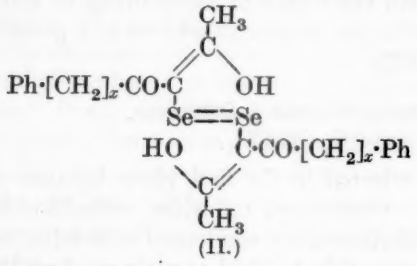
(I.)

or



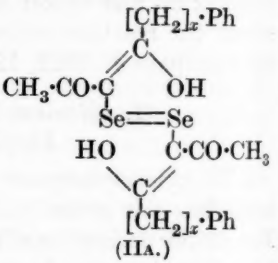
(IA.)

When reduced with hydriodic acid the two dimeric selenium β-diketones are converted respectively into *diselenium bis-ω-phenylacetylacetone* (II or IIA, $x = 1$) and *diselenium bis-β-phenylpropionylacetone* (II or IIA, $x = 2$). These characteristic derivatives, which are orange-coloured oils, are also formed in small quantities as by-products in the original condensation; their enolic character is manifested by the property of yielding ferric and copper salts.



(II.)

or

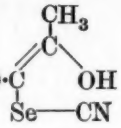


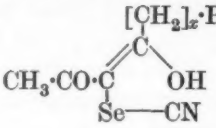
(IIA.)

This reduction with hydriodic acid appears, therefore, to be a general reaction and the same is true of the decomposition brought about by anhydrous hydrocyanic acid (2 mols.), each dimeric selenium β-diketone yielding quantitatively two molecular proportions respectively of *cyanoselenium ω-phenylacetylacetone* (III or IIIA, $x = 1$) and *cyanoselenium* β-*phenylpropionylacetone* (III or IIIA,

* In order to economise space the following graphic formulæ are generalised so as to represent both series of selenium derivatives. The formulæ of the phenylacetylacetone series contain only one CH_2 group ($x = 1$) within the square brackets, whereas those of the phenylpropionylacetone series include two CH_2 groups ($x = 2$).

$x = 2$). Both products when freshly prepared are colourless, crystalline, and enolic, but the latter is by far the more permanent.

(III.) 

(IIIA.) 

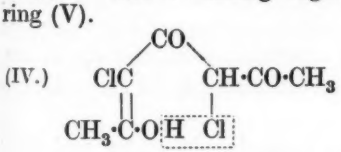
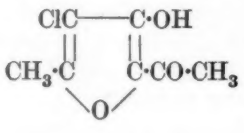
In the foregoing diagrams alternative formulæ have been indicated throughout because of the ambiguity attaching to the mode of enolisation of the parent β-diketones.

II. *Selenium Tetrachloride and Diacetylacetone.*

The interaction of selenium tetrachloride and diacetylacetone in the form of its barium salt has been studied because of the anomalous result obtained with this triketone and tellurium tetrachloride. In the latter case, condensation to dimethylpyrone occurred, and this product combined with the tellurichloric acid simultaneously formed to give rise to dimethylpyrone tellurichloride (this vol., p. 750).

Selenium tetrachloride reacts with this triketone mainly as a dehydrating and chlorinating agent; the principal organic product is 3 : 5-*dichloro*-2 : 6-*dimethylpyrone*, a considerable proportion of the selenium being eliminated in the elemental condition.

The dichlorodimethylpyrone is not obtained by direct chlorination of barium diacetylacetone, this procedure yielding mainly *trichlorodiacetylacetone*, a substance devoid of enolic properties. On treatment with barium hydroxide, 3 : 5-dichlorodimethylpyrone undergoes a remarkable change, half the chlorine is removed as hydrogen chloride, and the organic product is an enolic substance belonging to the furan series and probably 3-*chloro*-5-*acetyl*-4-*hydroxy*-2-*methylfuran* (V); its formation being due to alkaline hydrolysis of the dichloropyrone to dichlorodiacetylacetone, the latter then reacting with baryta in its monoenolic form (IV) to lose hydrogen chloride with a linking together of the open chain into a furan ring (V).

(IV.)  (V.) 

EXPERIMENTAL.

I. *Selenium ω-Phenylacetylacetone* (I or IA).

ω-Phenylacetylacetone (Fischer and Bülow, *Ber.*, 1885, **18**, 2137) was prepared by the Claisen condensation using ethyl phenylacetate

(3 mols.), dried acetone (1 mol.), and sodium (1 atom), and isolated as the greenish-blue copper derivative, this compound being washed successively with water and ether, the latter solvent removing a bright green, amorphous by-product (yield of copper salt 50 per cent.). When a smaller excess of ethyl phenylacetate was employed in the Claisen condensation, the proportion of green, tarry by-product was increased.

Copper ω-phenylacetylacetone, a light blue salt, was practically insoluble in water or petroleum and only sparingly soluble in alcohol or ether; it dissolved readily in chloroform and less in benzene or acetone; from benzene, it separated in felted masses of needles decomposing to a brown paste at 223—224°.

ω-Phenylacetylacetone, set free from the copper salt by 2*N*-sulphuric acid (yield 77 per cent.), boiled at 141—143°/15 mm. or with partial decomposition at 266—269°/750 mm.

The dried and powdered copper ω-phenylacetylacetone (27·2 grams = 1 mol.) was added gradually to 14·3 grams of selenium tetrachloride (1 mol.) in 70 c.c. of chloroform at 0°. After 30 minutes, cupric chloride was removed and the red filtrate evaporated to dryness in a current of air. After washing with alcohol and ether, 12 grams of light yellow residue were left consisting of crude *selenium ω-phenylacetylacetone* (yield 74 per cent.). The alcoholic and ethereal extracts were evaporated and the residue was extracted with petroleum (b. p. 80—100°). The final residue, a brown tar, contained other ill-defined selenium compounds; the petroleum extract, when shaken with copper acetate, gave 5·6 grams (55 per cent.) of the copper derivative of 3-chloro-ω-phenylacetylacetone, which was, however, contaminated by seleniferous products. Purification was effected by repeated crystallisation from benzene and by setting free the chloro-diketone with acid, extracting with ether, and regenerating the copper derivative with cupric acetate.

Copper 3-chloro-ω-phenylacetylacetone separated from benzene in light green, felted needles melting to a green liquid at 176—177° (Found : Cl = 14·51. $C_{22}H_{20}O_4Cl_2Cu$ requires Cl = 14·68 per cent.).

This copper derivative, which was soluble in the ordinary organic media, yielded, with mineral acid, 3-chloro-ω-phenylacetylacetone, as a colourless oil which could not be obtained solid in ordinary freezing mixtures.

Selenium ω-phenylacetylacetone was insoluble in water and only sparingly soluble in alcohol or ether; it dissolved more readily in acetone, chloroform, benzene, or glacial acetic acid, separating from the last three solvents in pale yellow plates, becoming pink on exposure to light. About 0·3 gram dissolved in 100 c.c. of cold benzene, but its solubility was seven times as great in the boiling

solvent. After repeated crystallisation from chloroform and benzene, it sintered at 161° and melted at 164—165° [Found: C = 52·69, 51·75; H = 4·11, 3·97; Se = 30·83; M = 516 by the ebullioscopic method in benzene (c = 1·97). $C_{22}H_{20}O_4Se_2$ requires C = 52·18; H = 3·95; Se = 31·23 per cent.; M = 506·2].

Selenium ω-phenylacetylacetone developed no coloration with ferric chloride, but red selenium separated on warming with 3N-sodium hydroxide or with mineral acid.

Diselenium Bis-ω-phenylacetylacetone (II or IIA).—Powdered selenium ω-phenylacetylacetone suspended in water and ether was reduced by 30 per cent. hydriodic acid (2·5 mols.). After removing with thiosulphate the iodine which had been liberated quantitatively, the orange ethereal solution was concentrated in a vacuum. Rapid evaporation caused partial crystallisation of the orange diselenium bis-ω-phenylacetylacetone, which, however, became oily again at the ordinary temperature (yield 90 per cent.). This orange-yellow oil developed an intense red coloration with ferric chloride and formed a brown copper derivative decomposing at 150—152°.

Cyanoselenium ω-Phenylacetylacetone (III or IIIA).—Three grams of powdered selenium ω-phenylacetylacetone were dissolved in 4 c.c. of freshly distilled hydrogen cyanide and 11 c.c. of anhydrous ether and after 2 hours the solution was evaporated in a vacuum; the snow-white residue was dried on porous tile and rapidly crystallised from petroleum (b. p. 40—60°), when *cyanoselenium ω-phenylacetylacetone* crystallised in colourless needles melting to a colourless liquid at 63—64° [Found: N = 5·23; M = 268 by cryoscopic method in benzene (c = 1·82). $C_{12}H_{11}O_2NSe$ requires N = 5·00 per cent.; M = 280]. Even when pure, this cyano-derivative slowly changed into a red tar, impurities hastening this decomposition; it was insoluble in water, but very soluble in organic media. With ferric chloride, it developed a dull red coloration and gave a light green copper derivative with cupric acetate.

II. *Selenium* β-*Phenylpropionylacetone* (I or IA).

β-Phenylpropionic acid was esterified by refluxing 124 grams with 250 c.c. of alcohol containing 15 grams of hydrogen chloride, when 115 grams of ethyl β-phenylpropionate were obtained boiling at 238—240° (yield 78 per cent. of the organic acid employed).

In the Claisen condensation to form β-phenylpropionylacetone, 7 grams of sliced sodium were added to 17·7 grams of acetone, 159 grams of the ester (3 mols.), and 150 c.c. of benzene, and in 12 hours the mixture had set to a semisolid mass containing only a minute quantity of metallic sodium.

The product was shaken with ice-water and benzene, when the

latter solvent removed the greater part of the excess of ethyl β-phenylpropionate. After partial neutralisation with acetic acid, the aqueous layer was treated with one-quarter of the calculated amount of cupric acetate, which precipitated the greyish-blue copper β-phenylpropionylacetone. Excess of cupric acetate added to the filtrate gave a bright bluish-green precipitate of the copper diketone and copper β-phenylpropionate. These two salts were partly separated by benzene extraction in a Soxhlet apparatus, when the former dissolved leaving the greater part of the sparingly soluble copper β-phenylpropionate. The total yield of copper diketone was 23·2 grams or 35 per cent. of theory.

Copper β-phenylpropionylacetone separated from benzene in light blue, matted crystals, m. p. 157—159° (Found: Cu = 14·52. $C_{24}H_{26}O_4Cu$ requires Cu = 14·40 per cent.).

On extraction with 2*N*-sulphuric acid and ether the crude copper salt gave 80 per cent. of the calculated amount of diketone boiling at 164—166°/16 mm. In order to characterise this diketone 2 grams of sodium *iso-p*-nitrobenzenediazo-oxide dissolved in 16 c.c. of glacial acetic acid were added gradually with stirring to 1·9 grams of the β-diketone in 40 c.c. of water and 3 c.c. of 5*N*-sodium hydroxide, an additional 50 c.c. of this alkali being run in during the coupling in order to keep the diketone in solution.

p-*Nitrobenzeneazo-β-phenylpropionylacetone*,

$$NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C(CO{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5){:}C(OH){\cdot}CH_3,$$

thus obtained in 70 per cent. yield, was sparingly soluble in petroleum, but crystallised well from acetone, alcohol, or glacial acetic acid in dark yellow needles, m. p. 131—132° (Found: C = 63·51; H = 5·43; N = 12·55. $C_{18}H_{17}O_4N_3$ requires C = 63·72; H = 5·02; N = 12·39 per cent.).

Eight grams of crude copper β-phenylpropionylacetone (4 mols.) dissolved in 30 c.c. of chloroform were shaken with 3 grams of selenium tetrachloride for ½ hour. After the solvent had been removed in a current of air, the yellow, oily residue deposited crystals on treatment with alcohol. After washing with alcohol and ether, the product A weighed 2·2 grams (61 per cent. of theory). The alcoholic and ethereal washings, on concentration in a vacuum, left a little more selenium compound (A) and an orange, tarry residue.

3-*Chloro-β-phenylpropionylacetone*, a colourless oil, was obtained from this tar by dissolving in benzene and precipitating fractionally with petroleum (b. p. 40—60°), the selenium compounds (B) being deposited first. The oily chlorinated diketone was transformed into copper salt by shaking with ether and cupric acetate (yield 42 per cent.). This copper derivative was purified by repeated crystallisation from carbon tetrachloride and benzene and by setting free

the chloro-diketone and again forming the metallic salt, which consisted of light green, matted crystals sintering at 191° and melting at 194—196° (Found: Cl = 13·48. $C_{24}H_{24}O_4Cl_2Cu$ requires Cl = 13·89 per cent.).

The first crops (A) of seleniferous products consisted mainly of *selenium* β-*phenylpropionylacetone*, which crystallised from benzene in pale yellowish-white leaflets sintering at 128° and melting at 141—142° [Found: C = 53·73; H = 4·57; Se = 29·39; M = 515 by ebullioscopic method in benzene (c = 1·58). $C_{24}H_{24}O_4Se_2$ requires C = 53·91; H = 4·49; Se = 29·65 per cent.; M = 534·4].

Selenium β-phenylpropionylacetone is non-enolic, giving no coloration with ferric chloride; it was more soluble than selenium ω-phenylacetylacetone in organic media; with benzene at comparable temperatures, the solubility was five times as great.

Diselenium bis-β-*phenylpropionylacetone* (II or IIA), an enolic substance, was present in the seleniferous products (B) precipitated by petroleum and identified therein by conversion into its copper derivative (m. p. 147—149°); it was prepared as an orange oil from selenium β-phenylpropionylacetone by reduction with hydriodic acid (p. 1273), the calculated amount of iodine being liberated. Its buff-coloured *copper* derivative from this preparation melted at 152—153° and did not depress the melting point of the foregoing specimen.

Cyanoselenium β-*phenylpropionylacetone* (III or IIIA) was prepared by dissolving 1 gram of selenium β-phenylpropionylacetone in 4 c.c. of freshly distilled hydrocyanic acid and 16 c.c. of ether. On evaporation the product was obtained in quantitative yield; it was very soluble in organic media and crystallised from petroleum (b. p. 40—60°) in colourless needles, m. p. 59—61° [Found: N = 4·83; Se = 26·70; M = 290, cryoscopic method in benzene (c = 1·27). $C_{13}H_{13}O_2NSe$ requires N = 4·76; Se = 26·91 per cent.; M = 294·2].

Cyanoselenium β-phenylpropionylacetone was much more stable on keeping than cyanoselenium ω-phenylacetylacetone; it developed a red ferric coloration and gave a greenish-yellow copper derivative having no definite melting point.

III. *Interaction of Selenium Tetrachloride and Barium Diacetylacetone.*

To 12.4 grams of selenium tetrachloride (5 mols.), suspended in 45 c.c. of chloroform B.P. at −10°, were added gradually 12·7 grams of dry powdered barium diacetylacetone (4 mols.) and after shaking for 45 minutes the calculated amount of barium chloride was deposited without any separation of selenium. The orange

filtrate, evaporated in a vacuum, left a small amount of selenium and a red oil which quickly became crystalline on washing with ether. By extraction with chloroform, this residue was separated into 3 grams of selenium (65 per cent. of calculated amount) and 5·6 grams of chlorinated pyrone (64 per cent.). The ethereal washings deposited a red tar consisting of inorganic and organic selenium derivatives from which no definite product could be obtained.

3 : 5-*Dichloro*-2 : 6-*dimethylpyrone*, $\begin{matrix} ClC\cdot CO\cdot CCl \\ \| \quad\quad \| \\ MeC\text{–}O\text{–}CMe \end{matrix}$, soluble in most organic media, dissolved only sparingly in light petroleum. Its solubility in hydrochloric acid was considerably greater than that in water, but the original substance separated from the acid solution. It crystallised well from benzene in white needles, m. p. 148—150°, and distilled unchanged at higher temperatures (Found : C = 43·69; H = 3·22; Cl = 36·51. $C_7H_6O_2Cl_2$ requires C = 43·52; H = 3·11; Cl = 36·73 per cent.). Towards acids, 3 : 5-dichloro-2 : 6-dimethylpyrone was remarkably stable, only 85 per cent. of its chlorine being removed by boiling for several hours with fuming nitric acid, but it was much more sensitive to the action of alkalis. Complete decomposition occurred with strong caustic alkalis and with baryta a more definite reaction was observable. On heating on the water-bath, 3·5 grams of 3 : 5-dichloro-2 : 6-dimethylpyrone with 12 grams of hydrated barium hydroxide, the organic reagent dissolved to a yellow solution from which an almost colourless barium salt then separated. On decomposing this barium compound with cold dilute hydrochloric acid and ether, the ethereal extract yielded 1·8 grams of a crystalline furan derivative. The yellow filtrate from the barium salt, which contained barium chloride as well as the organic salt, gave on acidification a further 0·8 gram of the organic product, the total quantity amounting to 82 per cent. of the calculated amount.

3-*Chloro*-5-*acetyl*-4-*hydroxy*-2-*methylfuran* (VII) developed a red ferric coloration and gave a bright green copper salt; it was appreciably volatile in air at the ordinary temperature and very volatile in steam. Sparingly soluble in water, it dissolved very readily in organic media, crystallising from light petroleum in long, colourless needles sintering at 80° and melting at 83—84° [Found : C = 48·16; H = 4·22; Cl = 20·45; M = 174·5, cryoscopic method in benzene (c = 0·91). $C_7H_7O_3Cl$ requires C = 48·15; H = 4·01; Cl = 20·32 per cent.; M = 174·5].

A yellow solution was produced on dissolving this furan derivative in warm 5N-sodium hydroxide, the sodium salt separating on cooling. Chlorine was readily removed from the compound by boiling with nitric acid.

The bright green *copper* derivative, which was soluble in chloroform or benzene, turned brown at 170°, and decomposed at 255—260°. A proximate analysis, made by decomposing this copper salt with sulphuric acid and ether, gave Cu = 15·49 and organic residue = 83·5 from ethereal extract. $Cu(C_7H_6O_3Cl)_2$ requires Cu = 15·49, organic residue = 85 per cent.

Trichlorodiacetylacetone, $CH_3{\cdot}CO{\cdot}CCl_2{\cdot}CO{\cdot}CHCl{\cdot}CO{\cdot}CH_3$.—An attempt to prepare the preceding 3 : 5-dichloro-2 : 6-dimethylpyrone by direct chlorination of barium diacetylacetone suspended in chloroform at 0° led to precipitation of the calculated amount of barium chloride, the deposition being completed by evaporating off the solvent. The residue consisted also of an oil which became partly crystalline after several weeks. It was freed from a considerable proportion of tar by repeated fractional precipitation from benzene by the addition of light petroleum. Trichlorodiacetylacetone, purified by crystallisation from light petroleum, separated in needles, m. p. 105—106° (Found : C = 33·96; H = 3·28; Cl = 43·44. $C_7H_7O_3Cl_3$ requires C = 34·23; H = 2·85; Cl = 43·27 per cent.). This trichloro-derivative gave no coloration with ferric chloride.

The authors desire to express their thanks to the Government Grant Committee of the Royal Society and to the Advisory Council of the Department of Scientific and Industrial Research for grants which have partly defrayed the expense of this investigation.

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CLVII.—*The Action between Bromine and Malonic Acid in Aqueous Solution.*

By RALPH WINTON WEST.

DURING his investigation of keto-enol tautomerism, K. H. Meyer (*Ber.*, 1912, **45**, 2864), on somewhat scanty evidence, arrived at the conclusion that the reaction between bromine and malonic acid was independent of the concentration of the former, and was of the unimolecular type indicated by the scheme

$$\cdot CH_2{\cdot}CO\cdot \xrightarrow{\text{slow}} \cdot CH{:}C{\cdot}OH \xrightarrow{\text{rapid}} \cdot CHBr{\cdot}CBr{\cdot}OH \xrightarrow{\text{rapid}} \cdot CHBr{\cdot}CO.$$

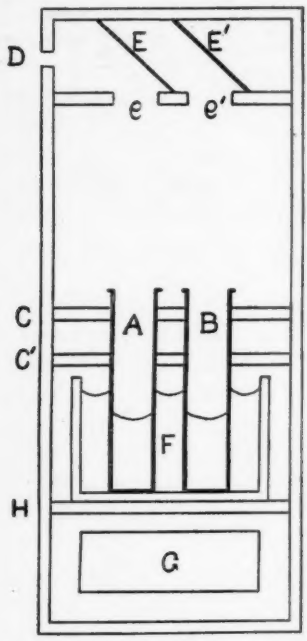
Thus the measurable stage consisted in the slow change from the keto to the enol form of the acid, which was brominated almost instantaneously.

Having regard to the general behaviour of malonyl compounds

towards bromine, it did not seem possible that the kinetics of the reaction could be as simple as Meyer's results would indicate, and therefore a more detailed investigation was undertaken.

Experimental.

Bromomalonic acid, even at low dilutions, reacts rapidly with acid solutions of potassium iodide, rendering direct volumetric estimation of the free bromine impossible. Methods involving the removal of excess bromine by the addition of readily brominated substances (phenols, etc.), and the subsequent estimation of the bromomalonic acid by means of potassium iodide, gave low and irregular results, due apparently to interaction between the "bromine remover" and the product of the reaction of the bromo-acid with the potassium iodide.



The reaction was followed colorimetrically in a modified form of tintometer. The apparatus consisted of a black box, three sides being constructed of wood, and the fourth left open but protected from light by a velvet curtain. *A* and *B* were 12 inch "Nessler" tubes of even bore, and showed less than 0·5 per cent. deviation in the height of a column of 50 c.c. of liquid. The tubes were held in alignment by the bored shelves *C* and *C′*, and rested on the glass bottom of the bath, *F*, which was supported by the glass shelf, *H*. *E* and *E′* were pieces of very thin mirror cut from the same piece of glass and fixed at an angle of 45° from the horizontal. The positions of *E* and *E′* over the circular holes *e* and *e′* were such that, when viewed through *D*, each mirror reflected half of its corresponding hole, forming a divided circle. Diffused light from an evenly illuminated ground glass screen was directed up the tubes by the tilted mirror, *G*.

The temperature of the bath was maintained at 0° throughout the whole series of experiments. Standard tints were prepared representing different points on the reaction curve. As it had been ascertained that hydrobromic acid caused a marked diminution in the colour of the bromine solution, each standard tint was composed of a solution of bromine in water to which had been added the quantity

of hydrobromic acid formed during the progress of the reaction to the measured point. The first standard was placed in position, the malonic acid and bromine solutions were mixed at 0°, and the reaction tube was fixed in the apparatus. The time of equalisation of tint was observed and the standard tube then changed. The experiments were carried out in quadruplicate, two readings being taken with the reaction tube in each of the positions *A* and *B*.

The bromine was purified by treatment with potassium bromide and zinc oxide, dried over lime, and distilled. The aqueous solutions were freshly prepared and were standardised every hour.

In the preliminary experiments it was found that :

(*a*) Hydrobromic acid had no influence on the reaction. It had been thought possible that the reaction would be governed by the presence of bromine in the ionised state or of tribromide-ions; but if this were so, the concentration of the hydrobromic acid would have a decided effect on the velocity of reaction.

(*b*) The rate of removal of bromine was approximately proportional to the concentration of the malonic acid, suggesting that the reaction is unimolecular with regard to this component.

(*c*) Alteration in the bromine concentration had a marked effect on the rate of bromination of the malonic acid. The figures obtained, however, had no simple significance; the velocity varying as a fractional power of the bromine concentration, and the index varying according to the range over which the velocities were compared. This variation with the bromine concentration suggests that the reaction must consist of at least two consecutive reactions, and it might well be that the bromomalonic acid is being further brominated to dibromomalonic acid.

Action of Bromine on Bromomalonic Acid.—When malonic acid is brominated in ether solution as described by Conrad and Reinbach (*Ber.*, 1902, **35**, 1816), although the product gives correct figures on analysis, it contains malonic acid and dibromomalonic acid as impurities. If, however, the ether solution of the crude acid is washed three times with water, on evaporation in a vacuum and drying over potassium hydroxide and then over phosphoric oxide, it yields pure bromomalonic acid, m. p. 113° (Found : Br = 43·77. Calc., Br = 43·71 per cent.).

The reaction between bromomalonic acid and bromine is symmetrically influenced by an equivalent excess of either constituent, and is of the bimolecular order.

The reaction is very rapid, and so will exert a considerable influence as a stage in the consecutive reactions involved in the bromination of malonic acid.

If the complete reaction were represented by two stages, the first

TABLE I.

Conc. of bromomalonic acid = Conc. of bromine = 0·01446 gm.-mol/.litre; $k = x/at(a - x)$.

t (mins.).	$a - x$.	k.	t (mins.).	$a - x$.	k.
0	0·01446	—	8·29	0·00964	4·17
2·5	0·01253	4·26	11·2	0·00868	4·11
4·2	0·01157	4·11	14·3	0·00771	4·23
6·05	0·01060	4·16	19·1	0·00674	4·15
				Mean	4·17

being independent of the bromine and the second dependent thereon, the condition that the velocity shall vary as a fractional power of the bromine concentration would be fulfilled. To test this supposition, it is necessary to determine the velocity coefficient for the inital period of the reaction. In order to minimise interference due to interaction between the bromomalonic acid and bromine, the concentration of the latter was reduced to the lowest effective value. In Table II are given the results of a typical experiment together with a summary of the other figures obtained.

TABLE II.

Concentration of malonic acid = 0·030 gm.-mol./litre.
Concentration of bromine = 0·00661 gm.-mol./litre.

t (mins.).	Conc. of acid.	$1/t$. log. $a/(a - x)$.
0	0·0300	—
1·92	0·0289	0·0084
3·83	0·0278	0·0086
5·92	0·0267	0·0085

No. of determinations, 14. Variation, 0·0081—0·0087. Mean value of k, 0·0085.

If a and b are the initial concentrations of malonic acid and bromine, and if after a time t, x and y denote the amounts of malonic acid and of bromomalonic acid transformed, then the rate of transformation of malonic acid is given by

$$-dx/dt = k_1(a - x) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and the rate of formation of dibromomalonic acid is given by

$$dy/dt = k_2(x - y)(b - x - y) \quad . \quad . \quad . \quad (2)$$

Equation (1) can be integrated and, knowing the values of a and k_1, the values of x can be calculated for each unit of time. From equation (2), for a small unit interval of time,

$$\delta y = k_2(x_1 - y_1 - \delta y/2)(b - x_1 - y_1 - \delta y/2) \quad . \quad . \quad (3)$$

where x_1 is the average value of x over the period, $y_1 = \Sigma\delta y$ up to the beginning of the period, and δy is the increase in y over the period.

Equation (3) is readily solved for δy and, taking the unit of time as 1 minute, the theoretical curve for the reaction can be plotted with a tolerable degree of accuracy.

In Table III the experimental results are compared with the calculated values as read from the theoretical curve.

TABLE III.

Concentration of malonic acid = 0·030 gm.-mol./litre.
Concentration of bromine = 0·03294 gm.-mol./litre: $k_1 = 0{\cdot}0085$; $k_2 = 4{\cdot}17$.

t (mins.).	Bromine ($\times 10^3$) used in the reaction ($x + y$). Found.	Calc.	Unimol. vel. coeff.	t (mins.).	Bromine ($\times 10^3$) used in the reaction ($x + y$). Found.	Calc.	Unimol. vel. coeff.
3·75	2·67	2·62	0·0108	21·5	16·02	16·20	0·0154
7·25	5·34	5·43	0·0117	25·75	18·69	19·00	0·0164
10·25	8·01	7·77	0·0132	30·0	21·36	21·50	0·0180
13·83	10·68	10·58	0·0138	39·0	26·70	25·91 *	0·0246
17·41	13·35	13·25	0·0147				

* $x = 0{\cdot}01602$; $y = 0{\cdot}00989$.

In the last column, values for a unimolecular velocity coefficient are expressed. These are of interest in view of Meyer's exposition of the kinetics of the reaction.

Conclusion.

The agreement between the found and calculated values for $(x + y)$, the bromine absorbed, is sufficiently good to justify the conclusion that the action of bromine on malonic acid is represented by the two consecutive reactions:

(1) a unimolecular reaction—the formation of bromomalonic acid—and

(2) a bimolecular reaction—the formation of dibromomalonic acid.

That stage (1) is unimolecular would indicate that the measured velocity is the slow transformation of the keto into the enolic form of the acid, and that the subsequent bromination is very rapid. Thus the scheme set out by Meyer (*loc. cit.*) does, in fact, represent the true mechanism, although it was based upon a wrong conception of the kinetics of the reaction.

The mechanism of stage (2) cannot, however, be deduced with such certainty. Bromomalonic acid still possesses a tautomeric hydrogen atom, and as enolisation takes place in (1), it would seem logical to assume that a similar change takes place in (2). Should such be the case, it is evident that the rate of enolisation must be rapid compared with the rate of bromination. It is possible that

the strain introduced at the central carbon atom by the bromine atom is such that the tendency for enolisation to take place is greatly increased. Such a strain would also make it more difficult to introduce the second bromine atom, and hence the bromination would be a relatively slow bimolecular reaction.

(2) $\cdot CHBr\cdot CO\cdot \xrightarrow{\text{rapid}} \cdot CBr{:}C\cdot OH\cdot \xrightarrow{\text{slow}} \cdot CBr_2\cdot CBr\cdot OH\cdot \xrightarrow{\text{rapid}} \cdot CBr_2\cdot CO.$

The condition of (2) would be equally well satisfied by the assumption that it is the keto-form of the acid which reacts with the bromine, but it is difficult to see how the analogy for the tautomerism of the acid is to be neglected.

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CLVIII.—*The Periodic Catalytic Decomposition of Hydrogen Peroxide.*

By ERNEST SYDNEY HEDGES and JAMES ECKERSLEY MYERS.

IN a previous communication (this vol., p. 604) the authors described the periodic catalysis of a number of reactions involving the liberation of hydrogen by the dissolution of metals in various reagents. The former paper also contains a bibliography of the work which has been done by Bredig and others on the periodic decomposition of hydrogen peroxide by mercury. It was shown that although many metals, after being heated in a vacuum or subjected to other kinds of treatment, induced periodicity in the metal–acid systems, mercury was normally active and caused the system to react in a periodic manner. This seemed to indicate that the periodic function of the mercury was fundamentally the same, both in its action on hydrogen peroxide and on the metal–acid systems, and therefore it was anticipated that some of the other metals which had been used as activating agents would, after treatment, have a periodic action on hydrogen peroxide.

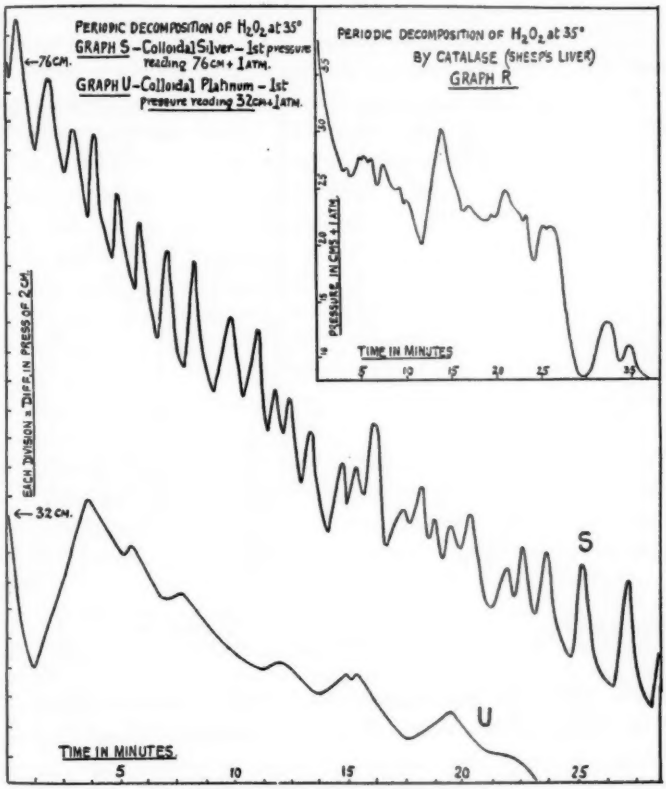
EXPERIMENTAL.

The methods of experimentation and the apparatus used are described in the former paper: in brief, the method is to register continuously the pressure of the gas as it is evolved. As, in general, the rate of evolution of gas was slower than in the former experiments and the amplitude of the waves rather less, it was found convenient in the majority of cases to follow the change by readings on the aniline manometer rather than by means of the self-recording

apparatus. In all the graphs shown, readings were taken every 15 seconds.

Mercury.—Previous investigators (*loc. cit.*) have traced the periodic catalysis of hydrogen peroxide by mercury to the golden oxide film which is observed to form periodically over the surface of the mercury. The present authors have observed the formation of this film under conditions when the evolution of oxygen was not

FIG. 1.

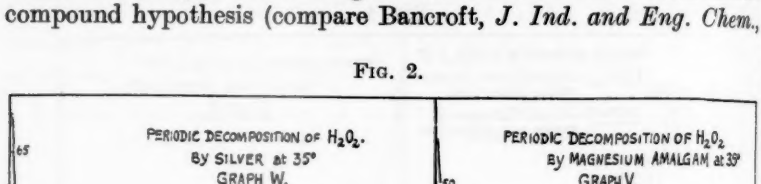

PERIODIC DECOMPOSITION OF H_2O_2 at 35°
GRAPH S – Colloidal Silver – 1st pressure reading 76 CM + 1 ATM.
GRAPH U – Colloidal Platinum – 1st pressure reading 32 CM + 1 ATM.
← 76 CM.
← 32 CM.
EACH DIVISION = DIFF. IN PRESS OF 2 CM.
TIME IN MINUTES.
5
10
15
20
25
S
U
PERIODIC DECOMPOSITION OF H_2O_2 at 35°
BY CATALASE (SHEEP'S LIVER)
GRAPH R
PRESSURE IN CMS + 1 ATM.
TIME IN MINUTES

periodic, and in fact this state of affairs has been the most easily realised. On the other hand, a periodic evolution of gas has been obtained in presence of gelatin when no visible film formed over the mercury, but this is a comparatively rare occurrence. They are therefore inclined to the view that the seat of the periodicity is much deeper and regard the alternate formation and dissolution of the film observed by most investigators as a result rather than a cause. Moreover, the film mentioned by Lemoine (*Compt. rend.*,

1916, **162**, 580), using 100-volume hydrogen peroxide, is black or brown, not golden. That the periodicity is of a more fundamental nature than has been supposed is also suggested by the observation of the present authors that although the frequency decreases slowly but regularly throughout an experiment, the amplitude of the waves rises and falls in a marked periodic manner.

The case is of some importance in the theory of catalysis, since it is sometimes quoted as an argument in favour of the intermediate-compound hypothesis (compare Bancroft, *J. Ind. and Eng. Chem.*,

FIG. 2.



1922, **14**, 326). It has been treated from a mathematical standpoint by Okaya (*Proc. Phys. Math. Soc. Japan*, 1919, [iii], **1**, 283).

New Cases of Periodic Catalysis.

In the examples which follow, the use of the term "positive" signifies that the evolution of oxygen from hydrogen peroxide was periodic. The term "negative" denotes a steady decomposition.

Copper.—Finely divided electrolytic: negative. Positive after heating and cooling three times in succession in a vacuum. Solution made acid (approximately $N/2$) by addition of hydrogen chloride so that conditions might resemble as closely as possible those under which activated copper was known to induce periodicity

in other systems. Reduced copper negative, whether heat-treated or not. Behaviour varies according to method of preparation. Copper reduced from cupric chloride by aluminium produced vigorous decomposition at first, falling off very quickly. Copper reduced from acidified copper sulphate by magnesium hypochlorite steadily increased in activity for a long time, reaching a maximum and ultimately falling off slowly. This initial increase in catalytic activity was also observed in some experiments using copper amalgam.

Silver.—Ordinary finely divided silver: negative, whether heat-treated or not. Positive when freshly prepared by reduction of an ammoniacal solution of the nitrate by sodium potassium tartrate, hydrazine sulphate, or hydroxylamine sulphate. Graph W represents an experiment using silver reduced by hydrazine sulphate. Positive result from silver prepared by adding hydrogen peroxide to an ammoniacal solution of silver nitrate. Silver obtained by heating the oxide in a vacuum, and a silver mirror reduced by Rochelle salt: both negative.

Alloys.—An alloy of copper and aluminium, which was previously described as dissolving periodically in hydrochloric acid after being melted in air, was found to evolve oxygen periodically from hydrogen peroxide after this treatment.

Metallic Couples.—Positive results from couples of magnesium and copper and of iron and zinc. The case is analogous to the employment of second metallic components in the dissolution of zinc or magnesium in hydrochloric acid, since either of these two metals alone gives a negative result with hydrogen peroxide. Positive results from silver–manganese and copper–manganese couples. Manganese alone: negative. Second metallic components activated by scraping the surface heavily.

Mercury Couples and Amalgams.—Pure mercury on neutral hydrogen peroxide produces very slow decomposition. A rapid and periodic evolution of oxygen ensues on dropping a piece of aluminium on to the surface of the mercury. Aluminium alone: negative. The case therefore resembles the periodic effect produced by mercury in the dissolution of aluminium in hydrochloric acid. Positive result from a magnesium–mercury couple: Graph V was obtained using a liquid amalgam prepared by dissolving metallic magnesium in warm mercury. Amalgams of lead and silver: negative. In none of these cases was the formation of any film over the surface of the mercury observed.

Colloidal Metals.—Freshly prepared colloidal platinum (by reduction of chloroplatinic acid or by sparking between two platinum electrodes under "conductivity" water): positive, whether pro-

tected by gelatin or not. Positive results also from colloidal silver and gold. Graphs U and S represent experiments with colloidal sols of platinum and silver respectively. Negative results from colloidal platinum which has been standing for 3 days. This is an extremely significant fact in the light of the experiments concerned with the ageing of colloids mentioned in the authors' former paper. Formaldehyde has on this system a toxic effect analogous to the action it exerts on the metal–acid systems. Direct addition of formaldehyde to the hydrogen peroxide systems does not inhibit the waves, because it is immediately oxidised, but the platinum or silver sol can be poisoned by formaldehyde before addition to the hydrogen peroxide.

This case recalls the experiments of Groll (*Kolloid Z.*, 1917, **21**, 168), who found that test samples withdrawn from colloidal sols of platinum or gold varied in their activity towards hydrogen peroxide, the activity varying periodically with time of withdrawal (compare also Rocasolano, *Anal. Fís. Quím.*, 1921, **19**, 114).

Carbon.—Cocoanut charcoal, with or without vacuum-heat treatment: negative. Firth and Watson, however (J., 1923, **123**, 1750) describe irregularities in the evolution of oxygen from hydrogen peroxide when decomposed by pure sugar carbon which has suffered heat-treatment in a vacuum. Poor, positive results have been obtained by the present authors with slightly alkaline colloidal carbon in the form of "aqua-dag."

Catalase.—Sheep's liver, whole ox-blood, or ox-blood corpuscles: positive. Catalase of potato or cabbage: negative. In the positive cases, ageing phenomena are again in evidence. After keeping for a few days, the liver gave a negative result, and no periodicity was observable when the corpuscles were 3 days old. Other instances of periodicity in enzyme action are cited by Groll (*Kolloid Z.*, 1917, **21**, 168) in the action of urease towards urea, and by Sluiter (*Ned. Tijdschr. Geneeskunde*, 1922, **66**, 572) in the activity of lipase towards milk.

Metallic Oxides.—Ordinary cupric oxide, with or without vacuum-heat treatment: negative. Cupric oxide prepared by boiling copper sulphate with an insufficiency of caustic soda and washing the product so as to avoid contamination with alkali gave a positive result. The product was still positive after keeping under water for 7 days, but gave a negative result when dried in the steam-oven. Freshly prepared cuprous oxide or barium dioxide: positive. Old material taken from stock: negative. Manganese dioxide, freshly prepared or not: negative.

Iodine.—Small irregular variations, disappearing when the conditions of reaction are, as in the other systems, made heterogeneous,

by addition of solid matter (compare this vol., p. 616). This is probably a supersaturation effect, since the irregularities do not persist under the conditions of heterogeneity prevalent in the periodic systems (compare, however, Bray, *J. Amer. Chem. Soc.*, 1921, **43**, 1262).

Platinum black, finely divided iron or cobalt, with or without vacuum-heat treatment: negative. All the experiments were conducted at 35°, and 20-volume hydrogen peroxide has been used throughout. The material used in some of the experiments contained a little free hydrochloric acid, but this did not appear to affect the results. During the course of this work, no specific influence of the reaction vessel, such as was described in the paper on metal–acid systems, has been observed. The investigation is at present being extended by studying the potential difference between the catalyst and the hydrogen peroxide solution.

Summary.

The periodic mercury–hydrogen peroxide catalysis is discussed and it is shown that the oxide film theory does not appear to meet the case. Consideration of the conditions under which periodic catalysis has been observed by the authors has led to the design of experiments intended to correlate this case with their experiments on metal–acid systems. A periodic decomposition of hydrogen peroxide can be effected by finely divided copper after vacuum-heat treatment and by silver obtained by certain methods of reduction. Some amalgams exert a periodic action, and certain metallic couples after one of the metals has been subjected to one of the methods of activation. The catalytic effect on solutions of hydrogen peroxide of colloidal platinum, gold, and silver and of catalase is periodic and in these instances the ageing phenomena described by the authors for the colloid systems in a previous paper were observed. Certain freshly precipitated metallic oxides have a periodic catalytic action on hydrogen peroxide.

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CLIX.—*The Heat of Adsorption of Oxygen by Charcoal.*

By Ernest Alfred Blench and William Edward Garner.

The adsorption of oxygen by charcoal and its subsequent removal from the surface by the action of heat or high vacua have been studied over a wide range of temperatures. Dewar (*Proc. Roy. Soc.*, 1904, A, **74**, 122) found that oxygen adsorbed on charcoal at the temperature of liquid air could be recovered without change on raising the temperature. McLean (*Trans. Roy. Soc., Canada*, 1921, **15**, 73) and other workers, in experiments at the ordinary temperature, have shown that oxygen, carbon monoxide, and carbon dioxide may be present in the gases removed by heating or evacuation. Above 200°, on the other hand, no oxygen can be pumped off as such, even on raising the temperature, the gases evolved consisting entirely of oxides of carbon. The ratio of carbon monoxide to dioxide rises as the temperature increases (Rhead and Wheeler, J., 1913, **103**, 461). These and other results show clearly the dependence of the products of desorption on the temperature, and indicate that radical differences exist between the adsorption processes at low and high temperatures.

The heats of adsorption and desorption have been less thoroughly studied. Dewar found a value of 3 Cal./mol. at −185°, and McLean has made a few measurements at the ordinary temperature. In the present work, the heats of adsorption of oxygen on charcoal between 20° and 450° have been determined.

Since the commencement of this investigation, F. G. Keyes has communicated to us the results of experiments at 0°. For infinitely small volumes of oxygen adsorbed, he finds that the heat of adsorption is 70 Cal., but when the surface is nearly saturated with oxygen the heat liberated amounts to only 4 Cal. The former value agrees with our measurements at 18° within experimental error.

The difficulties of measuring heats of reaction at high temperatures are accentuated in the case of the adsorption of oxygen on charcoal by the formation of carbon monoxide and dioxide. In the main, these difficulties have been overcome, as will be seen from the experimental part of this paper, but great accuracy is not claimed for the experimental results so far obtained; for example, the heat of adsorption given for 300° may be up to 15 per cent. too low or 3 per cent. too high. The heats of adsorption summarised below (Table I) thus possess a qualitative rather than a quantitative significance. In this table are given the volumes of oxygen adsorbed by 4—5 grams of charcoal previously exhausted at 900°, and the heat of adsorption per gm.-mol. of oxygen adsorbed. The heat

for small quantities of oxygen adsorbed on a bare carbon surface rises with increase in temperature from 52 Cal. at 18° to 224 Cal./mol. at 450°. Above 200° the heat of adsorption is greater than the heat of formation of carbon dioxide. Only one value has been obtained at 200° and two at 450°.

TABLE I. Heat of Adsorption between 18° and 450°.

$T°$	18	199	283	450
C.c. adsorbed	1·299	1·331	1·295	0·593
Heat of ads. in Cal./mol.	52	115	154	224

The heat of adsorption at any one temperature is the greater the smaller the volume of gas admitted to the bare surface. The results at 18° illustrate this point (see also Table II).

C.c. of oxygen ads.	1·761	1·299	0·958
Heat of ads in Cal./mol.	49	52	64

As would be expected, in view of this result, the heat of adsorption decreases as successive quantities of oxygen are adsorbed on the carbon surface (Tables II, III, and IV). An exception occurs at 450°; the heat for the second is larger than for the first admission of oxygen.

The significance of the large temperature coefficient of the heat of adsorption is not immediately clear. It is necessary to consider the above measurements in conjunction with the detailed investigation of the adsorption process made by Rhead and Wheeler (*loc. cit.*), of which a brief statement will be given. These workers have found that it was impossible, at the temperature of adsorption, to remove any of the adsorbed oxygen from a carbon surface by evacuation at low pressures. This holds for temperatures above 200°. On raising the temperature and still maintaining the vacuum, a fraction of this gas was evolved, but temperatures above 900° were necessary for its complete removal. The residue not removed after continued exhaustion at any temperature is considered by them to be present on the surface in the form of a complex (C_xO_y) in which the oxygen atoms or molecules are held to the surface by the attraction of several carbon atoms.

An extension of this idea to the behaviour of individual groups of carbon and oxygen atoms provides a simple explanation of the high temperature coefficient of the heat of adsorption. The stabilities and heats of formation of the individual groups will be affected by the manner in which the oxygen atoms are oriented on the irregular carbon surface, and those groups will be stable at any particular temperature which possess a heat of formation greater than a certain critical value. The higher the temperature the greater will be the heat of formation of a stable group. It would

therefore be anticipated that the heat of adsorption would rise with the temperature.

The occurrence of three products of desorption, oxygen, carbon monoxide, and dioxide, points to at least three modes of attachment on the carbon surface. The oxygen may be held as molecular oxygen with none of its primary valencies broken. This would appear to be the mode of attachment at −185°, for not only is oxygen recovered on desorption, but also the heat of adsorption is very low, *e.g.*, 2—4 Cal./mol. On the other hand, it may be held as O_2 with one of its valencies broken, or as oxygen atoms.

We suggest that the formation of these and similar groups of atoms accounts for the phenomena observed when oxygen is adsorbed by carbon, and it is hoped that more accurate investigations of the energy changes involved will give a clearer insight of the whole mechanism of the process.

Experimental.

Materials.—Charcoal. A vegetable carbon, "Norite," was sieved and that portion remaining on a 150-mesh sieve was purified by treatment with hydrofluoric and hydrochloric acids, the ash content being thereby reduced from 7 to 0·2 per cent. Water and adsorbed gases were expelled before each experiment by heating at 900°, in a vacuum of 1×10^{-4} mm. for several hours. The same sample of charcoal was used throughout this investigation.

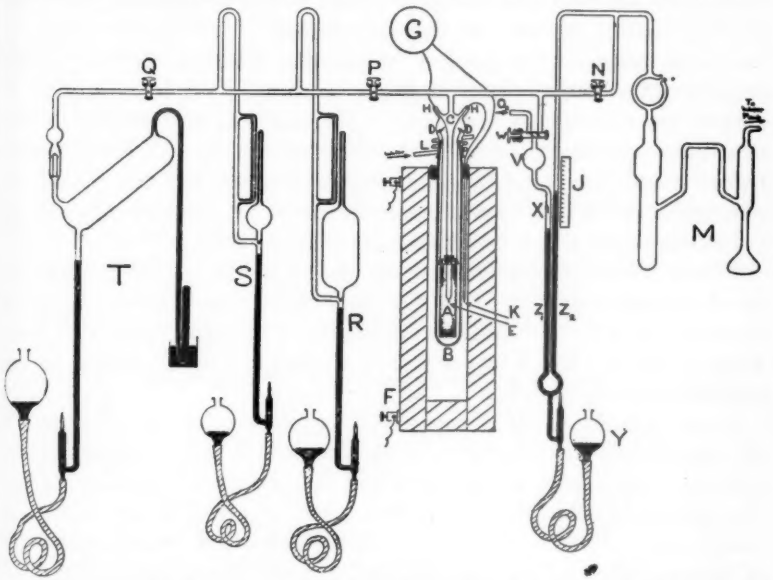
Gases.—The oxygen was obtained by heating potassium permanganate, and dried over phosphorus pentoxide. The helium was kindly given to us by Dr. Irvine Masson, and had been purified over charcoal at the temperature of liquid air.

Apparatus.—The complete apparatus, shown in the diagram, consists of an adsorption vessel, condensation pumps for evacuation, and apparatus for measuring temperatures, pressures, and volumes, and for collecting and analysing the gases produced.

The adsorption vessel (enlarged in the diagram relatively to the other parts of the apparatus) was a quartz tube, *B*, fused at one end, and closed at the other by a ground stopper, *C*. It could be heated at temperatures between room temperature and 1000° in the electric furnace, *F*. The carbon was placed in a cylindrical vessel, *A*, of 200-mesh platinum gauze, which, whilst retaining the charcoal particles, allowed easy passage of gas to the interior. The platinum gauze container, which weighed 4·98 grams, was suspended from the glass hooks, *DD*, in the stopper, *C*. The stopper was kept cool by water circulating through the lead tube, *L*. The temperature of the electric furnace around *B* was measured by a thermocouple, not shown in the diagram. The rise in temperature of the charcoal

during an experiment was measured by a second thermocouple, the "hot" junction of which, *E*, was embedded in the carbon, and the "cold" junction, *K*, was maintained in the space between the quartz tube, *B*, and the tubular electric furnace, *F*. This thermocouple was used in conjunction with a Campbell standard galvanometer, *G*, and was calibrated in the neighbourhood of 20°, 100°, 200°, 300°, and 450° against standard thermometers, by inserting the two junctions in constant-temperature baths.

The adsorption vessel was evacuated by means of the mercury diffusion pumps, *M*, through the stopper, *C*, by way of the tap, *N*, and communicated through the tap *P* with the McLeod gauges, *R*



and *S*, one of which was used for low and the other for relatively high pressure measurements. The McLeod gauges were connected with a Topler pump, *T*, by which samples of gas could be withdrawn from the apparatus for analysis.

Gas was admitted from a burette, consisting of a bulb, *V*, and a U-tube, Z_1Z_2. The volume of *V* from the tap *W* to the pointer, *X*, was accurately determined to $\pm$ 0·03 in 27 c.c. Z_2 was permanently in connexion with the high vacuum pumps, and hence the pressure of the gas in *V* could be read off directly by measuring the difference between the levels of the mercury in Z_1 and Z_2. This was read on the scale, *J*, by means of a telescope.

The "Gas Effect."—To determine the volumes of gas required to fill the dead space in the adsorption vessel, *B*, McLeod gauges,

and connecting tubes, known volumes of oxygen or other gases were admitted to the evacuated apparatus, with the adsorption vessel at temperatures between 20° and 450°. The "equivalent volume" of the apparatus was deduced from the change of pressure measured. It was noticed during this operation that the temperature in *B* rose one or two degrees, and remained at a new level as long as the pressure of the gas was constant. It fell to its original value after removal of the gas. The rise in temperature, which is called the "gas effect," was independent of the pressure of the gas for pressures above 0·03 cm. Owing to the presence of the large cooled stopper, *C*, a temperature gradient in the adsorption vessel was unavoidable, and alterations in this gradient occurred on introduction of gas into the evacuated vessel. The rise in temperature was the same for oxygen, carbon dioxide, and helium within experimental error. Two methods were adopted to eliminate or correct for this rise in temperature, (1) admission of helium to the evacuated apparatus and measurement of rise in temperature before admitting oxygen (pressure of helium, 0·5 cm.), and (2) admission of carbon dioxide, measurement of rise in temperature, exhausting apparatus, and then admitting oxygen.

Introduction of Helium to eliminate the "Gas Effect."—Dry charcoal (4—5 grams) was heated in the adsorption vessel at 900° under a vacuum of 1×10^{-4} mm. for 2 hours. The taps *N* and *P* were then closed and the temperature of the furnace was lowered to the experimental temperature.

First Admission of Oxygen.—After admission of helium, a measured volume of oxygen (approximately 1 c.c.) was introduced into the vessel, and the temperature read every 10 seconds. After the maximum had been reached, usually after 25 seconds, the middle tap, *P*, was opened for 10 seconds, and about four-fifths of the gas taken off into the McLeod gauges. Readings of the temperature, then slowly falling, were continued every 15 seconds for a few minutes. The pressure of the gas in the McLeod gauges was then read, and a sample analysed for carbon monoxide, dioxide, oxygen, and helium.

The uncorrected rise in temperature due to the combination of oxygen with carbon was taken to be the difference between the maxima on the temperature curves for the admissions with helium and oxygen.

To calculate the heat evolved, the rise in temperature, corrected for radiation, was multiplied by the water equivalent of the substances undergoing the rise in temperature. The specific heat of carbon at the ordinary temperature was taken as 0·165 (Weber, *Pogg. Ann.*, 1875, **154**, 557), while at higher temperatures it was

assumed to be 0·003 higher than that of graphite (*ibid.*, and also Mills, *J. Physical Chem.*, 1917, **21**, 350). The water equivalent of the carbon at 300° was about 1·4 cal./degree and that of the platinum about 0·16 at the same temperature.

The heat liberated is the sum of that due to the adsorption and to the production of carbon monoxide and dioxide. Corrections were made for the heats of formation of the gaseous products.

Volume Adsorbed.—Since no carbon monoxide was present in the gaseous products, the volume adsorbed is the difference between the volume of oxygen admitted and the volume of gases present in the adsorption vessel at the time of maximum temperature. The heat liberated per gm.-mol. of oxygen adsorbed is given in Table II.

Second Admission of Oxygen.—After the readings for the first admission of oxygen had been taken, the apparatus was evacuated for ½ hour without raising the temperature, helium and oxygen were successively admitted, and the heat of adsorption on a partially saturated surface was obtained. Sometimes a third admission was carried out in a similar manner.

First, second, and third admissions are denoted in the tables by suffixes i, ii, and iii respectively.

Table II gives the results of these experiments, with the data necessary for the calculation of the heat of adsorption. The volumes are measured at the temperatures given in column 2.

TABLE II. Experiments with preliminary admission of helium.

Expt. No.	Temp. of atmosphere.	Temp. of carbon.	Equivalent volume. C.c.	Vol. of helium admitted. C.c. at 76 cm.	Vol. of oxygen admitted. C.c. at 76 cm.	Pressure at max. temp. Cm.	Vol. of oxygen adsorbed. C.c. at 76 cm.	Vol of CO_2 produced. C.c. at 76 cm.	Rise of temp.	Time to max. temp. Secs.	Heat evolved (corr. CO_2). Gm.-cals.	Heat of adsorption. Cals. per mol. adsorbed.
Ai	20°	335°	470	0·848	3·090	0·256	2·356	0·60	10·2°	10	13·63	139
Aii	„	298	474	1·148	2·808	0·308	2·038	0·49	3·9	15	4·13	49
Bi	„	304	473	1·086	1·212	0·226	0·891	0·29	4·5	30	5·88	159
Ci	17	310	473	0·975	1·058	0·192	0·838	0·13	3·7	30	5·56	158
Cii	„	304	473	1·086	1·785	0·240	1·379	0·36	4·5	15	5·96	103
Ciii	„	305	473	1·502	1·785	0·283	1·527	0·12	4·0	30	6·09	95
Di	18	304	473	1·295	1·025	0·244	0·801	0·13	3·8	30	5·72	170
Ei	19	310	473	1·387	0·978	0·266	0·710	0·12	3·4	25	5·09	172
Eii	„	305	473	1·343	1·542	0·303	1·001	0·13	4·6	25	7·03	168
Eiii	„	300	474	1·270	1·418	0·286	0·904	0·29	3·0	30	3·77	100
Hi	17	450	461	1·491	1·174	0·342	0·593	0·32	3·7	20	5·57	224
Hii	„	457	460	1·476	1·346	0·366	0·606	0·39	4·9	20	7·52	295
Ki	16	199	487	1·138	1·555	0·210	1·345	0·07	4·7	20	6·45	114
Kii	17	193	487	0·441	1·403	0·095	1·235	0·10	2·4	20	3·05	59

TABLE III.

Expt. No.	Temp. of atmosphere.	Temp. of carbon.	Equivalent volume. C.c.	Vol. of oxygen admitted. C.c. at 76 cm.	Pressure at max temp. Cm.	Vol. of oxygen adsorbed. C.c. at 76 cm.	Vol. of CO_2 produced. C.c. at 76 cm.	Rise of temp. (corr. for radn. and gas effect).	Time to max. temp. Sec.	Heat evolved (corr. for CO_2). Gm.-cals.	Heat of adsorption. Cals. per mol. adsorbed.
Ni	18°	297°	453	1·558	0·032	1·367	0·10	5·75°	25	10·15	177
Nii	„	288	454	1·839	0·044	1·577	0·13	4·85	30	8·44	128
Pi	19	283	455	1·546	0·042	1·295	0·13	4·8	30	8·36	154
Pii	18	272	456	1·507	0·036	1·291	0·10	4·0	25	7·00	129
Qi	19	294	454	1·645	0·047	1·365	0·14	3·5	15	5·92	104
Qii	18	292	454	1·540	0·045	1·272	0·14	3·3	20	5·50	103

Wt. of carbon 4·79 grams. Mean for first admissions 145.
Mean for second admissions 120.

Heat is not liberated uniformly throughout the mass of carbon, and the results with the thermocouple in one position can only be relative. It would appear, however, that a thermocouple placed in the middle of the mass records a rise in temperature which is approximately the mean temperature.

The results of experiments at 18° are shown in Table IV.

TABLE IV.

Exp. No.	Temp. of carbon.	Vol. of O_2 admitted.	Vol. of O_2 adsorbed. C.c.	Vol. of CO_2 produced. C.c.	Rise in temp. Corr.	Heat evolved. Gm.-cals.	Heat of ads. Cal./mol.
Ri	18°	2·260	1·761	—	4·29°	3·64	49
Rii	„	2·716	0·442	—	0·71	0·60	32
Si	„	2·158	1·299	—	3·30	2·81	52
Sii	„	2·302	0·320	—	0·27	0·23	17
Ti	14·5	1·331	0·958	—	3·02	2·61	64
Tii	17	2·216	0·246	—	0·49	0·42	41

These experiments were carried out in the order given. The carbon was not replaced throughout the series except that after Bi a small loss of carbon was made good by the addition of fresh material. The weight of dry carbon from Ai to Bi was 4·02 grams, and from Bi to Kii, 4·20 grams. For both the carbon dioxide and oxygen admissions, the final readings on the temperature–time curves were identical within experimental error. Thus the gas effect was undoubtedly the same for both gases. In a series of experiments at 18°, there was no gas effect, so admission of carbon dioxide was unnecessary.

The heat of adsorption under given conditions is not appreciably affected by repeated treatment of the carbon surface with oxygen. It

is thus unlikely that any of the heat liberated was due to the heat of combustion of gases adsorbed on the surface of charcoal.

The rise in temperature obtained on the admission of oxygen to the charcoal was due to the superposition of two effects, (i) heat gained from the walls (gas effect) and (ii) heat of reaction. It can be shown that the corrected rise in temperature is approximately $(T_c - T_{CO_2})T_g/T_{C_2}$, where T_c and T_g are the maximum rises in temperature due to the admission of oxygen (corrected for radiation) and the gas effect, respectively, and T_{CO_2} and T_{O_2} the increases in temperature in 5 seconds for the carbon dioxide and oxygen admissions. The rise in temperature given in Table III has been corrected in this manner.

For expts. N, P, and Q, the thermocouple was $1\frac{1}{2}$, 3, and $4\frac{1}{2}$ cm., respectively, from the top of the carbon, and the total height of the carbon particles was 6 cm.

Weight of carbon from Ri to Tii, 4·21 grams. At these temperatures, no carbon dioxide is evolved after the introduction of oxygen to the carbon surface.

Summary.

The heat of adsorption of oxygen by charcoal for the first small quantities of oxygen adsorbed ranges from 60 to 220 Cal./mol. of oxygen adsorbed as the temperature of adsorption rises from 18° to 450°, and falls off rapidly as the surface becomes saturated.

The rapid rise in the heat of adsorption is ascribed to changes in the mode of orientation of the oxygen atoms on the surface with temperature. At low temperatures, oxygen molecules are adsorbed without chemical change, but at high temperatures intimate combination occurs with the formation of groups C_xO_y on the surface. Some of these groups are stable and others unstable at any particular temperature. The heat of formation of the stable groups increases with increase in the temperature of adsorption.

Our thanks are due to the Chemical Society for a grant for the purchase of apparatus, and to the Department of Scientific and Industrial Research for a grant to one of us (E. A. B.).

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UNIVERSITY COLLEGE, LONDON. [*Received, March 12th*, 1924.]

CLX.—*The Bromine Compounds of Phenanthrene. Part III.*

By HERBERT HENSTOCK.

THE bromination of phenanthrene-3-sulphonic acid and the sulphonation of 10-bromophenanthrene yield two isomerides (Sandqvist, *Annalen*, 1917, **417**, 1; *Ber.*, 1920, **53**, 13, 168). The bromination of phenanthrene-2-sulphonic acid by a similar method yielded an acid of the type $\begin{matrix} C_6H_4\cdot C{:}O \\ (2)SO_3H\cdot C_6H_3\cdot CHBr \end{matrix}$, the salts of which are highly coloured. These, however, rapidly lost their colour, owing to an internal rearrangement of the molecule producing salts corresponding to (I).

The sulphonation of 10-bromophenanthrene produced neither coloured substances nor any derivative of the 2-monosulphonic acid, but the bromination of phenanthrene-2-sulphonic acid by means of dry bromine vapour yielded a phenanthrene 9 : 10-dibromide 2-sulphonic acid, which on heating in the air lost a molecule of hydrogen bromide and at the same time absorbed oxygen.

$$\begin{matrix} C_6H_4\text{—}CHBr \\ (2)SO_3H\cdot C_6H_3\text{—}CHBr \end{matrix} \rightarrow \begin{matrix} C_6H_4\text{—}C\cdot OH \\ (2)SO_3H\cdot C_6H_3\text{—}CBr \end{matrix} \quad \text{(I).}$$

Whether the bromine is in position 9 or 10 was not determined.

The scarlet substance prepared by treating 2 : 10-dibromophenanthrene with boiling alcoholic potassium hydroxide (J., 1921, **119**, 59) has been further examined. After removal of an impurity, it gave analytical figures, which together with the formation of *p*-bromodiphenic acid on oxidation, and the intense colour of the substance (compare also Werner, *Annalen*, 1902, **322**, 135) suggest the constitution

$$\begin{matrix} C_6H_4\text{—}C{:}O^{-}O{:}C\text{—}C_6H_4 \\ (2)BrC_6H_3\text{—}C{=\!=\!=}C\text{—}C_6H_3Br(2) \end{matrix}$$

The substance refuses to yield an oxime and to undergo reduction, possibly on account of its sparing solubility in almost all solvents.

The above constitution for this substance gives a clue to the position of the second bromine atom in the dibromophenanthrene melting at 161° (described in Part I) which was there left undetermined.

EXPERIMENTAL.

Bromination of Potassium Phenanthrene-2-sulphonate.—An aqueous solution of potassium phenanthrene-2-sulphonate (5 grams in 500 c.c.) at 30° was treated gradually with 300 c.c. of bromine

water (saturated at 21°). After 12 hours, the bromine having been absorbed, about 0·5 gram of ammonium chloride (which seemed to stabilise the product for a short time) was added to the mixture, which was heated and made strongly alkaline with barium hydroxide, whereupon it slowly acquired a brilliant dark green colour; this faded on cooling and reappeared on boiling. The solid precipitated on the addition of sodium chloride was rapidly collected, washed with alcohol and with ether, and dried at about 50° for a few minutes. The brilliant dark green powder thus obtained could not be analysed, owing to its rapid decomposition. It did not melt below 250°, and was very soluble in water, forming a deep green solution, purple by transmitted light, which dyed cotton. The solid gradually turned light green, yellow, and finally brown, and the original colour could not be restored. If ammonium chloride was not added during the preparation, these changes occurred with kaleidoscopic rapidity. The brown powder was washed with water [Found: Ba = 16·04. $(HO{\cdot}C_{14}H_7Br{\cdot}SO_3)_2Ba$ requires Ba = 16·41 per cent.]. It had all the properties of the barium bromohydroxyphenanthrenesulphonate described below.

Similar results were obtained when sodium or potassium hydroxide was substituted for barium hydroxide.

The free *acid*, a bright blue, amorphous powder, was prepared by acidifying with hydrochloric acid an aqueous solution of the freshly isolated, green barium salt and adding sodium chloride to the brilliant, electric blue solution; it was dried in the same manner as the barium salt (Found: C = 47·08; H = 2·93. $C_{14}H_8OBr{\cdot}SO_3H$ requires C = 47·59; H = 2·55 per cent.).

The acid is very soluble in water, forming a bright blue solution which dyes cotton in the same shade. Even in solution, it is much more stable than the green barium or potassium salt and may be kept for 24 hours without change, whereas the salts decompose in less than 1 hour. Its colour gradually fades to a dull slate, and the acid is now less soluble in water, but unaltered in composition (Found: C = 47·13; H = 2·89 per cent.).

Bromination of Potassium Phenanthrene-2-sulphonate with Bromine Vapour.—Five grams of dry potassium phenanthrene-2-sulphonate were exposed, in a desiccator, to the vapour from 2·7 grams (1 mol.) of dry bromine, which was absorbed during 2 weeks. The orange-yellow granular product fumed in the air, giving off hydrogen bromide [Found: HBr = 17·03. $C_{14}H_9Br_2{\cdot}SO_3K$ requires HBr (1 mol.) = 17·76 per cent.]. The dibromide also lost one molecule of hydrogen bromide when heated at 100° for 2 hours and then at 150° for 1 hour; the brownish-white, hygroscopic residue (yield quantitative) separated from hot aqueous solution as a yellow,

amorphous powder, which was dried at 100° [Found: K = 9·53. $C_{14}H_7(OH)Br{\cdot}SO_3K$ requires K = 9·97 per cent.].

The *sodium* salt, prepared in a similar manner, is a brownish-white, hygroscopic, amorphous powder, which is more soluble in water than the potassium salt [Found: C = 44·14; H = 2·60. $C_{14}H_7(OH)Br{\cdot}SO_3Na$ requires C = 44·80; H = 2·10 per cent.].

The *silver* salt, obtained from the sodium salt and silver nitrate in faintly acid solution, is, when dry, a cream-coloured, amorphous powder [Found: C = 36·33; H = 2·20; Ag = 23·3. $C_{14}H_7(OH)Br{\cdot}SO_3Ag$ requires C = 36·52; H = 1·80; Ag = 23·40 per cent.]. It is readily soluble in hot water, insoluble in cold water, and darkens on exposure to light.

10-*Bromo*-9-*hydroxyphenanthrene*-2-*sulphonic Acid.*—A hot, aqueous solution of the silver salt was treated with hydrochloric acid, the silver chloride removed, and the filtrate evaporated, finally to dryness over solid sodium hydroxide in a vacuum desiccator, the *sulphonic acid* being obtained as a granular, white powder (Found: C = 47·49; H = 3·04. $C_{14}H_9O_4BrS$ requires C = 47·59; H = 2·51 per cent.). The aqueous solution of the acid, on treatment with concentrated hydrochloric acid, drop by drop, yields a clear, colourless, viscous jelly; the viscosity of this solution depends on the concentration of the hydrochloric acid, increasing at first and then diminishing. The jelly is double-refracting, consequently the acid belongs to Sandqvist's II series, and the bromine is in position 10. The hydroxyl group is probably in position 9.

The normal barium salt, prepared from the sulphonic acid and barium nitrate solution, is identical with that produced by the decomposition of the green dyestuff (p. 1297) (Found: Ba = 16·34 per cent.). The *basic barium* salt, obtained from the potassium salt in very faintly acid (nitric) solution by means of barium hydroxide, is similar to the normal salt, but is slightly soluble in water [Found: Ba = 26·74. $C_{14}H_7(OH)Br{\cdot}SO_3{\cdot}Ba{\cdot}OH$ requires Ba = 27·10 per cent.].

Two insoluble *lead* salts corresponding with (1) PbO and (2) Pb_3O_4 were produced by methods similar to those used in preparing the barium salts; lead acetate was the precipitant in both cases. (1) Found: Pb = 23·31. $[C_{14}H_7(OH)Br{\cdot}SO_3]_2Pb$ requires Pb = 22·72 per cent. (2) Found: Pb = 18·51. $[C_{14}H_7(OH)Br{\cdot}SO_3]_8Pb_3$ requires Pb = 18·76 per cent. They are both yellowish-white, amorphous powders soluble in dilute nitric acid.

The *ferric* salt, prepared by adding a slight excess of ferric chloride to a solution of the potassium salt acidified with dilute nitric acid, was obtained as a white precipitate which, on drying at 115°, changed to a dark brown, amorphous powder, quite insoluble in water, but

soluble in dilute acids [Found : Fe = 5·12. $\{C_{14}H_7(OH)Br\cdot SO_3\}_3Fe$ requires Fe = 5·08 per cent.].

After the ferric hydroxide had been removed in the analysis of the iron salt, a white precipitate of the *ammonium* salt formed in the filtrate on cooling. Dried at 100°, it was obtained as a white, amorphous powder, soluble in hot, but insoluble in cold, water [Found : NH_4 = 5·10. $C_{14}H_7(OH)Br\cdot SO_3NH_4$ requires NH_4 = 4·86 per cent.].

9 : 10-*Dibromophenanthrene-2-sulphonyl bromide* was prepared by heating potassium 10-bromo-9-hydroxyphenanthrene-2-sulphonate with phosphorus pentabromide and phosphoryl bromide at 135° for 20 minutes. The product was washed with water and recrystallised from benzene–alcohol and finally from hot alcohol, being obtained as a dull yellow, amorphous powder, m. p. 204° (Found : C = 35·55; H = 2·07. $C_{14}H_7Br_2\cdot SO_2Br$ requires C = 35·07; H = 1·67 per cent.).

Dibromodiphenanthraquinone.—The scarlet substance previously obtained (*loc. cit.*), after removal of a plum-coloured impurity, gave C = 61·42; H = 3·03; Br = 29·20 ($C_{28}H_{14}O_2Br_2$ requires C = 61·99; H = 2·58; Br = 29·59 per cent.). On oxidation with chromium trioxide in glacial acetic acid solution, *p*-bromodiphenic acid, m. p. 237—238°, was obtained (Found : C = 51·81; H = 3·10. Calc., C = 52·33; H = 2·80 per cent.). Schmidt and Junghans (*Ber.*, 1904, **37**, 3558) give the m. p. as 238—239°.

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SCHOOL GARDENS, SHREWSBURY. [*Received, March 11th*, 1924.]

CLXI.—*Sulphonation of* m-*Cresol and its Methyl Ether.*

By ROBERT DOWNS HAWORTH and ARTHUR LAPWORTH.

THE products obtained by sulphonation of *m*-cresol were first examined by Claus and Krauss (*Ber.*, 1887, **20**, 3089). A monosulphonic acid was formed by the action of concentrated sulphuric acid at 120° which gave crystalline salts and was shown to be *m*-cresol-6-sulphonic acid (Me : OH : SO_3H = 1 : 3 : 6), as it readily yielded *p*-toluquinone on oxidation. This acid corresponds with phenol-*p*-sulphonic acid, the more stable of the two isomerides formed when phenol is sulphonated.

By the action of a large excess of sulphuric acid at 120—140° on *m*-cresol, Claus and Krauss obtained a disulphonic acid and a trisulphonic acid which were isolated in the form of salts. The constitutions of these two acids were not determined by these workers, but there now can be no doubt that they were *m*-cresol-4 : 6-disulphonic acid and *m*-cresol-2 : 4 : 6-trisulphonic acid, respectively. The latter corresponds with phenoltrisulphonic acid in which the three hydrogens situated in the ortho- and para-positions with respect to the strongly directive hydroxyl group are all replaced. Claus and Dreher (*J. pr. Chem.*, 1889, [ii], **39**, 366) attempted to isolate *m*-cresol-2-sulphonic acid or *m*-cresol-4-sulphonic acid, which correspond with phenol-*o*-sulphonic acid, from the products obtained by sulphonation of *m*-cresol with sulphuric acid at low temperatures, but were not successful. It appeared somewhat remarkable that *m*-cresol should not yield a sulphonation product corresponding with phenol-*o*-sulphonic acid, and Mr. M. L. Wilson, in these laboratories, on making preliminary reinvestigation of the question, found that monosulphonation of *m*-cresol, either with sulphuric acid or with chlorosulphonic acid, usually leads to mixtures of two acids, the nature and proportions of which vary with the agent and the conditions employed during the sulphonation process; by fractional crystallisation of their salts a partial separation of the two acids was effected. One of these acids had properties very different from those of the true cresolsulphonic acids and was ultimately found to be identical with Verley's *m*-tolyl hydrogen sulphate, $C_6H_4Me{\cdot}O{\cdot}SO_3H$ (*Bull. Soc. chim.*, 1901, **25**, 46).

The view that phenylsulphuric acids are formed during the sulphonation of phenols, and even that they represent intermediate stages in the sulphonation process, was at one time widely held, receiving its principal support in the formation of the supposed β-naphthylsulphuric acid during the sulphonation of β-naphthol (Armstrong, *Ber.*, 1882, **15**, 202, 204, 207; Nietzki, *ibid.*, p. 305). Since the discovery that this compound was in reality 2-naphthol-1-sulphonic acid, the idea that phenylsulphuric acids may be formed in appreciable quantities during ordinary sulphonation of phenols has not been considered very seriously.

The authors have now found that the action of concentrated sulphuric acid on *m*-cresol results in the production of two monosulphonic acids which are readily separated by means of their barium salts. Endeavours to replace the sulphonic groups by the hydroxyl, cyano-, or amino-group were unsuccessful and in order to determine the constitutions of the monosulphonic acids, it was necessary to convert them into the corresponding methyl ethers by boiling in alkaline solution with methyl sulphate, and to com-

pare the products with the synthetic 3-methoxytoluenesulphonic acids which have been described in an earlier paper (Haworth and Lapworth, J., 1923, **123**, 2982). In this way, the less soluble barium salt has been identified as that of *m*-cresol-4-sulphonic acid, and the more soluble as that of Claus and Krauss's *m*-cresol-6-sulphonic acid. The relative amounts of these two acids varied according to the conditions employed for the sulphonation. When the sulphonation was carried out at 120°, the main product was the 6-sulphonic acid, but at lower temperatures considerable quantities of the 4-sulphonic acid could be obtained, although the total sulphonation was reduced.

When *m*-cresol was allowed to react in carbon disulphide solution with one molecular proportion of chlorosulphonic acid at — 15°, *m*-tolyl hydrogen sulphate was obtained together with *m*-cresol-6-sulphonic acid, the potassium salts of the two acids being readily separated and the yields being respectively 50 and 15 per cent. of those theoretically possible. *m*-Tolyl hydrogen sulphate could also be prepared in excellent yield by the action of chlorosulphonic acid on a carbon disulphide solution of *m*-cresol in presence of pyridine (compare Verley, *loc. cit.*). The authors could not detect the presence of *m*-cresol-4-sulphonic acid amongst the products obtained by the action of chlorosulphonic acid on *m*-cresol. Further, when the carbon disulphide was removed by distillation, and the mixture of *m*-tolyl hydrogen sulphate and *m*-cresolsulphonic acid heated on the steam-bath, the only product isolated was *m*-cresol-6-sulphonic acid, thus proving that the sulphonic group migrated from the hydroxyl group to the 6-position on warming.

m-Cresol-4 : 6-disulphonic acid was produced by the action of two molecular proportions of chlorosulphonic acid on a carbon disulphide solution of *m*-cresol, migration of the sulphonic group to the nucleus being ensured by removing the solvent and heating the residual oil at 100° for 4 hours. The *m*-cresoldisulphonic acid appeared to be identical with that prepared by Claus and Krauss (*loc. cit.*), and its constitution was proved in the usual manner by conversion to its methyl ether, which was identical with the 3-methoxytoluene-4 : 6-disulphonic acid prepared synthetically (Haworth and Lapworth, *loc. cit.*, p. 2991). Under the conditions of our experiments, no *m*-cresolmonosulphonyl chloride was produced, although it is well known that sulphonyl chlorides are produced by the action of two molecular proportions of chlorosulphonic acid on toluene (Claesson and Wallin, *Ber.*, 1879, **12**, 1848; Heumann and Kochlin, *Ber.*, 1882, **15**, 1118; Noyes, *Amer. Chem. J.*, 1886, **8**, 176). The presence of the hydroxyl group evidently renders the ortho- and para-standing hydrogen atoms so

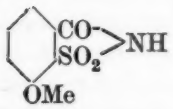
labile that the second molecule of chlorosulphonic acid replaces a second hydrogen atom in the benzene nucleus, in preference to attacking the sulphonic group already in the molecule.

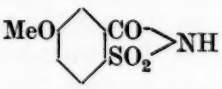
A third sulphonic group could not be introduced by the action of three molecular proportions of chlorosulphonic acid, only *m*-cresol-4 : 6-disulphonic acid being isolated.

The methyl ether of *m*-cresol (= *m*-tolyl methyl ether) was sulphonated in carbon disulphide at — 15° by means of chlorosulphonic acid and 3-methoxytoluene-6-sulphonic acid was isolated in good yield, but no other sulphonic acid could be detected.

The potassium salts of *m*-cresol-4- and -6-sulphonic acids were nitrated in glacial acetic acid solution and 6-nitro-*m*-cresol-4-sulphonic acid and 4-nitro-*m*-cresol-6-sulphonic acid respectively were obtained. The constitutions of these acids were determined by removing the sulphonic group with hydrochloric acid in sealed tubes, and identifying the resulting nitro-*m*-cresol.

We have examined the oxidation products of 3-methoxytoluene-4-, 6-, and 2-sulphonic acids. When the sulphonamides of the 2- and 6-sulphonic acids were oxidised by means of alkaline permanganate solutions, 3-*methoxy*-o-*benzoicsulphinide* (I) and 5-*methoxy*-o-*benzoicsulphinide* (II), respectively, were obtained, whilst the 4-sulphonamide was oxidised to 3-methoxy-4-sulphonamidobenzoic acid.

(I.) 



(II.)

The potassium salts of 3-methoxytoluene-4- and -6-sulphonic acids were also oxidised by means of alkaline permanganate and the potassium salts of 3-methoxy-4-sulphobenzoic acid and 3-methoxy-6-sulphobenzoic acid were produced. The former yielded 3-methoxy-4-sulphonamidobenzoic acid and the latter yielded 5-methoxy-*o*-benzoicsulphinide after treatment of the corresponding sulphonyl chlorides with ammonia.

EXPERIMENTAL.

Methylation of m-*Cresolsulphonic Acids.*—The sodium or potassium salt was dissolved in about ten times its weight of boiling water containing potassium or sodium hydroxide (2 mols.) respectively, methyl sulphate (1 mol.) was slowly added, and the solution boiled until a portion, when neutralised with mineral acid and treated with a few drops of ferric chloride solution, gave no violet coloration. The time required for completion of the process varied considerably.

Action of Concentrated Sulphuric Acid on m-*Cresol.*—*m*-Cresol, sulphonated with concentrated sulphuric acid for 1 hour at 30—35°, yielded the 4- and the 6-sulphonic acids in the ratio 1 : 2·7. When the sulphonation was carried out at 100° (steam-bath), the two acids were formed in the ratio 1 : 1·9; at 120°, after 1 hour's heating, the main product was the 6-sulphonic acid. No other products than these were detected.

Action of Chlorosulphonic Acid (1 *mol.*) *on* m-*Cresol* [with MAURICE LOWELL WILSON].—(*a*) *m*-Cresol (50 grams), dissolved in carbon disulphide (250 c.c.), was cooled to — 15°, and chlorosulphonic acid (55 grams) gradually added with vigorous stirring, the temperature being maintained below — 10°. After the resulting acids had been converted, through the barium salts, into potassium salts, and fractionated, the first fraction yielded potassium *m*-tolyl sulphate (35 grams) as white, nacreous plates. The second and third fractions were contaminated with potassium chloride, but potassium *m*-cresol-6-sulphonate (10 grams) was isolated by extracting the mixture with boiling alcohol; on concentration the potassium salt separated in long needles.

(*b*) *m*-Cresol (20 grams) was sulphonated as in experiment (*a*). The carbon disulphide was distilled and the remaining syrup heated for 4 hours on the steam-bath, after which it was dissolved in water, neutralised with barium hydroxide, filtered, and concentrated, when barium *m*-cresol-6-sulphonate (45 grams) separated.

(*c*) To a mixture of chlorosulphonic acid (22 grams), carbon disulphide (190 grams), and pyridine (30 grams), cooled to — 15°, *m*-cresol (22 grams) was slowly added, the temperature being maintained below — 10°. After 1 hour, the carbon disulphide was distilled, the residual syrup dissolved in water and made alkaline with potassium hydroxide, and the pyridine evaporated in a vacuum, when potassium *m*-tolyl sulphate separated (yield 70 per cent.).

Action of Chlorosulphonic Acid (2 *mols.*) *on* m-*Cresol.*—*m*-Cresol (20 grams), dissolved in carbon disulphide (100 c.c.), was cooled below 35° during the gradual addition of chlorosulphonic acid (44 grams). The carbon disulphide was distilled, the residual solid heated for 2 hours at 100° and finally dissolved in water, neutralised with barium hydroxide, and the solution filtered and concentrated, when barium *m*-cresol-4 : 6-disulphonate (66 grams) separated in crusts of white needles.

An attempt to prepare *m*-cresoltrisulphonic acid by the action of chlorosulphonic acid (3 mols.) on *m*-cresol, dissolved in carbon disulphide, led to the formation of the disulphonic acid, which was isolated as the barium salt. The weight of barium sulphate

confirmed the fact that one molecular proportion of chlorosulphonic acid had been inert.

Action of Chlorosulphonic Acid (1 *mol.*) *on* m-*Tolyl Methyl Ether* [with MAURICE LOWELL WILSON].—*m*-Tolyl methyl ether was sulphonated with chlorosulphonic acid as described for the sulphonation of *m*-cresol at −10° to −15° (p. 1303). Barium 3-methoxytoluene-6-sulphonate was obtained in good yield, but no isomeric compound could be detected.

Salts of m-*Cresol-6-sulphonic Acid* [with MAURICE LOWELL WILSON].—The *barium* salt, tufts of small needles, decomp. 180°, was soluble in water (34 grams in 100 grams at 17°) and was insoluble in cold but fairly soluble in boiling alcohol. Its aqueous solution gave a violet coloration with ferric chloride, rapidly decolorised bromine water, and was immediately oxidised by cold alkaline permanganate solution [Found : Ba = 25·0. $(C_7H_7O_4S)_2Ba,H_2O$ requires Ba = 25·1 per cent.]. The copper salt, green rods, was identical with that described by Claus and Krauss (*loc. cit.*). The *ammonium* salt crystallised in hexagonal prisms, the *ferrous* salt in pale green rods, and the *zinc* salt from concentrated solution in tufts of needles. The *potassium* salt, prepared from the barium salt, crystallised in long needles. It was soluble in hot alcohol and 17 grams dissolved in 100 grams of water at 18° (Found: K = 14·3. $C_7H_7O_4SK,2H_2O$ requires K = 14·3 per cent.).

The potassium salt on methylation yielded well-defined, square plates which were identical with a synthetic specimen of 3-methoxytoluene-6-sulphonic acid. The corresponding sulphonyl chloride (m. p. 23°), sulphonamide (m. p. 130°), and sulphonanilide (m. p. 104°) were identical with the synthetic compounds, no alteration in melting point being produced by admixture.

4-*Nitro*-m-*cresol-6-sulphonic Acid*.—The *potassium* salt, prepared by nitrating potassium *m*-cresol-6-sulphonate in acetic acid containing a few drops of acetic anhydride by means of 100 per cent. nitric acid, separated as a yellow precipitate, and recrystallised from water as pale yellow, rhombic prisms. Heated in a sealed tube with concentrated hydrochloric acid for 7 hours at 170°, it gave 4-nitro-*m*-cresol, m. p. 56°, which was isolated by steam distillation.

Salts of m-*Cresol-4-sulphonic Acid*.—The *barium* salt, rhombic plates, decomp. 150°, resembled the 6-sulphonate in the properties described. It was soluble to the extent of 4·5 grams in 100 grams of water at 20° [Found : Ba = 25·1. $(C_7H_7O_4S)_2Ba,H_2O$ requires Ba = 25·1 per cent.]. The *copper* salt crystallised from water in small, green rods. The *potassium* salt, elongated prisms from water, was soluble in hot alcohol and 9 grams dissolved in 100 grams of

water at 18° (Found: K = 17·1. $C_7H_7O_4SK$ requires K = 17·0 per cent.).

The potassium salt was methylated as described in the case of the corresponding 6-sulphonate, the product crystallising in long needles identical with potassium 3-methoxytoluene-4-sulphonate prepared synthetically. The corresponding sulphonyl chloride (m. p. 78°), sulphonamide (m. p. 169°), and sulphonanilide (m. p. 142°) were identical with the corresponding synthetic products, a conclusion confirmed by the mixed melting-point test.

6-*Nitro*-m-*cresol*-4-*sulphonic Acid*.—The potassium salt, prepared by nitrating potassium *m*-cresol-6-sulphonate as previously described for the 4-sulphonic acid, was fairly soluble in water, but could be recrystallised from this solvent as pale yellow needles. Hydrolysed in a sealed tube, it gave 6-nitro-*m*-cresol, m. p. 127°.

m-*Tolyl Hydrogen Sulphate*.—The salts of this compound are very different from those of the *m*-cresolsulphonic acids, being easily decomposed when boiled with dilute hydrochloric acid, giving no violet coloration with aqueous ferric chloride, and being stable to cold alkaline permanganate solution, although slowly oxidised on boiling.

Barium m-*tolyl sulphate* was obtained in indefinite, crystalline form. The corresponding *potassium* salt was sparingly soluble in cold water, decomposed slowly at 100°, and decolorised bromine water very slowly. A nearly quantitative yield of *m*-hydroxybenzoic acid was obtained from it as follows: an aqueous solution of the salt (5 grams) and potassium hydroxide (5 grams) at about 100° was treated gradually with 30 per cent. sodium permanganate (25 c.c.), oxidation occurring readily. The excess of permanganate was destroyed by alcohol, the filtered solution concentrated to 60 c.c., acidified with concentrated hydrochloric acid, and warmed for 1 hour in order to hydrolyse the sulphate group. On cooling, *m*-hydroxybenzoic acid separated from the solution as white needles, m. p. 200°.

Salts of m-*Cresol*-4 : 6-*disulphonic Acid*.—The *barium* salt, crusts of small crystals, was not very soluble in water and gave a ruby red coloration with ferric chloride (Found: Ba = 33·8. $C_7H_6O_7S_2Ba$ requires Ba = 34·0 per cent.). The potassium salt, prepared from the barium salt, was very soluble in cold water, from which it separated in small prisms, which in bulk possessed the mother-of-pearl appearance characteristic of the potassium salt of the 4 : 6-disulphonic acid described by Claus and Krauss (*loc. cit.*).

The potassium salt was methylated in the usual manner, but after boiling for 15 hours with a large excess of methyl sulphate and sodium hydroxide, a red coloration was still produced on

testing with ferric chloride. The solution was concentrated and the last fractions were extracted with hot alcohol. The alcohol was removed and the dried residue triturated with phosphorus pentachloride and poured into water. The oil was extracted with benzene, dried over potassium carbonate, and light petroleum was added, when 3-methoxytoluene-4 : 6-disulphonyl chloride was precipitated. On repeating the treatment with benzene and light petroleum, the compound was obtained in a pure state and melted at 111—112°, alone or mixed with synthetic 3-methoxytoluene-4 : 6-disulphonyl chloride.

3-*Methoxy*-6-*sulphobenzoic Acid* [with MAURICE LOWELL WILSON].—The *hydrogen potassium* salt was prepared by oxidising potassium 3-methoxytoluene-6-sulphonate (10 grams) in hot water (100 c.c.) with 1·6 per cent. potassium permanganate (900 c.c.) for 6 hours on the water-bath. The excess of permanganate was destroyed by addition of alcohol, the mixture filtered, concentrated to 50 c.c., and acidified with concentrated hydrochloric acid. The white crystals (5·5 grams) separated from hot water as white, rhombic plates which liberated carbon dioxide from a solution of sodium carbonate; they were dried at 150° for analysis (Found : K = 14·4. $C_8H_7O_6SK$ requires K = 14·4 per cent.).

5-*Methoxy*-o-*benzoicsulphinide* (II) [with MAURICE LOWELL WILSON].—Prepared either from the potassium salt described above by trituration with phosphorus pentachloride, followed by decomposition with ammonia, or by oxidising 3-methoxytoluene-6-sulphonamide with alkaline sodium permanganate on the steam-bath, the sulphinide was obtained by acidifying the alkaline solutions with hydrochloric acid, and recrystallised from acetone as long, white needles, m. p. 242°; it dissolved with effervescence in sodium carbonate solution and possessed a bitter taste (Found : C = 45·0; H = 3·5. $C_8H_7O_4NS$ requires C = 45·0; H = 3·3 per cent.).

3-*Methoxy*-4-*sulphobenzoic Acid*.—The *hydrogen potassium* salt was prepared by oxidising potassium 3-methoxytoluene-4-sulphonate as described above, and crystallised from water in rhombic plates which dissolved in sodium carbonate solution with effervescence (Found : in salt dried at 150°, K = 14·3. $C_8H_7O_6SK$ requires K = 14·4 per cent.).

3-*Methoxy*-4-*sulphonamidobenzoic acid* was prepared by triturating the potassium salt of 3-methoxy-4-sulphobenzoic acid with phosphorus pentachloride, and decomposing the oily sulphonyl chloride with ammonia. It was also prepared by oxidation of 3-methoxytoluene-4-sulphonamide with alkaline sodium permanganate. When the alkaline solutions were acidified with hydrochloric acid, the sulphonamidobenzoic acid separated in rhombic plates, m. p. 254—

255° (Found : C = 41·3; H = 4·1. $C_8H_9O_5NS$ requires C = 41·5; H = 3·9 per cent.).

3-Methoxy-o-benzoicsulphinide (I), prepared by oxidising the synthetic 3-methoxytoluene-2-sulphonamide with alkaline permanganate, crystallised from alcohol in white needles, m. p. 227—228° (decomp.). It dissolved in sodium carbonate solution with effervescence and possessed a bitter taste (Found : C = 45·1; H = 3·6. $C_8H_7O_4NS$ requires C = 45·0; H = 3·3 per cent.).

The authors desire to express their thanks to the Research Fund Committee of the Chemical Society for a grant from which some of the cost of this research was defrayed. One of us (R. D. H.) is indebted to the Commissioners of the 1851 Exhibition for a scholarship which has enabled him to participate in this research.

THE UNIVERSITY OF MANCHESTER. [*Received, March 18th,* 1924.]

CLXII.—*The Dissociation Pressures of Hydrated Double Sulphates. Part II. Various Double Sulphates of the Type* $M''SO_4,M'_2SO_4,6H_2O$.

By ROBERT MARTIN CAVEN and JOHN FERGUSON.

THE authors have shown (J., 1922, **121**, 1407) that the vapour pressures of the systems $CuSO_4,M'_2SO_4,6H_2O$–$CuSO_4,M'_2SO_4,2H_2O$ diminish with univalent metals in the order, K, Rb, Tl, NH_4, Cs. A conclusion drawn from those results regarding ammonium was subsequently elaborated by one of us (*Chem. and Ind.*, 1923, **164**, 448, 744), but was criticised by Moore (*ibid.*, 343, 641).

A number of measurements of vapour pressures of hydrated double salts have been made by Ephraim and Wagner (*Ber.*, 1917, **50**, 1088), including salts of the type $M''SO_4,M'_2SO_4,6H_2O$, where M'' = Cu, Ni, Mg, Mn, and M' = K, NH_4, Rb, Cs; but no means seem to have been taken by these authors to secure the presence of the lower hydrates which are necessary for equilibrium; and the results when expressed graphically reveal irregularities which we have not observed.

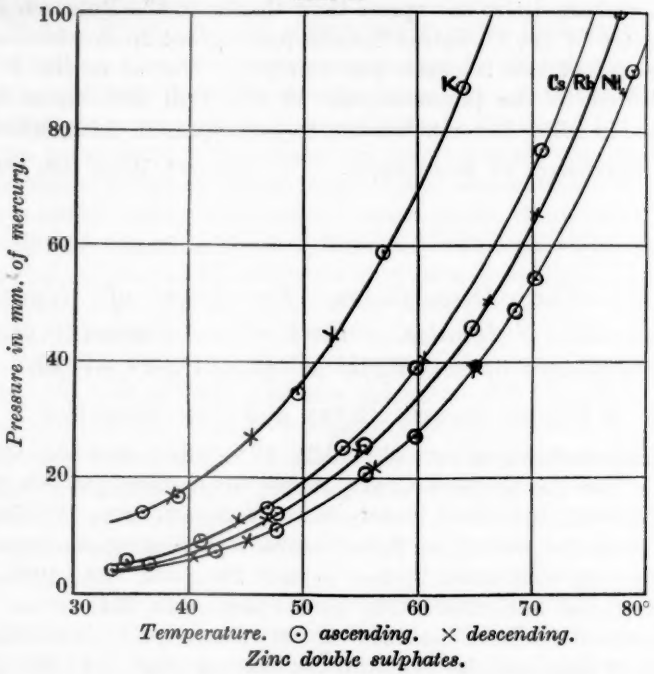
The vapour pressures of double sulphates of magnesium, zinc, cadmium, manganese, ferrous iron, cobalt, and nickel with the alkali metals have now been examined by us; and curves plotted from the values obtained with both ascending and descending temperatures are found to be quite regular, and can be expressed each by a single mathematical formula.

Experimental.

The apparatus and methods employed in the vapour-pressure measurements were those already described in Part I. The experimental results have been expressed by formulæ of the type $\log p = a + b/T - c/T^2$, where a, b, and c are constants.

In most cases, the formation of the lower hydrate by heating the hexahydrate in an air-oven showed the induction lag noted by Rae (J., 1916, **109**, 1229). For example, cobalt potassium sulphate,

Fig. 1.



Zinc double sulphates.

when heated for the first time, does not lose water until the temperature reaches 95°, dehydration yielding the violet anhydrous salt. On rehydration and a second heating, water is lost at as low a temperature as 80°, and the reddish-brown dihydrate is obtained, which is stable up to 100°. Dehydration in a desiccator yields also at first the violet anhydrous salt.

Estimations of sulphate and total water were carried out on each salt.

Cobalt Potassium Sulphate. $a = 6{\cdot}764$, $b = -265{\cdot}7$, $c = 451{,}350$.

Temp.	26·5°	32·8°	39·6°	45·7°	51·1°	57·0°	60·6°	66·3°	76·3°	66·2°	54·0°	27·6°
Press obs.	7·2	11·6	19·2	30·6	44·2	64·2	81·6	114·6	201·3	113·4	53·5	8·3
Press. calc.	7·0	11·6	19·8	30·7	44·3	65·1	81·7	115·1	201·3	114·3	53·6	7·7

Cobalt Rubidium Sulphate. $a = 3{\cdot}740$, $b = 1594$, $c = 762{,}740$.

Temp.	28·4°	33·3°	38·4°	45·3°	52·6°	58·9°	65·1°	76·1°	53·3°	35·8°	27·4°
Press. obs.	4·3	6·8	9·7	16·3	26·9	41·7	59·9	112·2	28·8	8·0	4·1
Press. calc.	4·3	6·4	9·9	16·5	27·7	41·4	60·2	111·0	28·8	8·0	4·0

Cobalt Cæsium Sulphate. $a = 8{\cdot}164$, $b = -1221$, $c = 313{,}270$.

Temp. ...	29·2°	41·0°	47·0°	53·8°	60·2°	75·0°	66·2°	58·8°	51·6°	43·1°
Press. obs.	5·1	12·2	19·6	31·3	47·6	118·6	70·1	44·0	26·5	15·0
Press. calc.	4·9	12·5	19·4	31·2	47·6	117·0	69·7	43·3	26·8	14·8

Cobalt Ammonium Sulphate. $a = 7{\cdot}600$, $b = 843{\cdot}4$, $c = 388{,}300$.

Temp.	35·3°	43·8°	50·7°	61·7°	67·3°	82·2°	54·0°	47·1°	37·5°
Press. obs. ...	5·7	11·8	19·3	41·2	58·7	140·9	25·0	15·5	7·2
Press. calc. ...	6·0	11·5	19·2	41·2	58·8	140·6	24·4	15·1	7·2

Nickel Potassium Sulphate. $a = 0{\cdot}981$, $b = 3329$, $c = 1{,}039{,}000$.

Temp.	33·8°	45·1°	55·8°	64·8°	76·2°	66·5°	60·8°	48·6°
Press obs. ...	6·2	14·6	31·2	54·6	98·1	59·6	42·8	19·4
Press. calc. ...	6·2	15·1	31·3	53·7	98·2	59·0	42·4	19·3

Nickel Rubidium Sulphate. $a = 10{\cdot}563$, $b = -2937$, $c = 44{,}740$.

Temp.	32·5°	40·1°	49·6°	58·3°	74·8°	67·1°	51·9°	34·4°
Press. obs. ...	3·0	5·5	10·5	19·9	55·7	35·2	12·9	3·5
Press. calc. ...	3·0	5·3	10·7	19·5	56·0	34·7	12·6	3·4

Nickel Cæsium Sulphate. $a = -1{\cdot}730$, $b = 4798$, $c = 1{,}249{,}600$.

Temp.	35·0°	44·2°	48·7°	55·9°	65·7°	82·0°
Press. obs. ...	4·8	9·0	12·6	18·9	35·4	75·2
Press. calc. ...	4·8	9·3	12·9	20·2	34·9	74·1

Nickel Ammonium Sulphate. $a = 2{\cdot}370$, $b = 2437$, $c = 946{,}400$.

Temp.	33·5°	43·2°	53·7°	68·0°	72·8°	64·1°	48·2°	40·9°
Press. obs. ...	1·6	4·1	9·2	24·3	31·9	18·6	5·7	3·4
Press. calc. ...	1·8	4·1	9·2	23·1	31·8	18·7	6·1	3·3

Zinc Potassium Sulphate. $a = 10{\cdot}834$, $b = -2992$, $c = 0$.

Temp.	35·9°	38·7°	49·2°	57·2°	63·4°	52·3°	45·4°	38·1°	16·2°
Press. obs. ...	14·1	16·6	34·2	59·6	87·1	44·4	27·3	16·2	3·6
Press. calc. ...	14·1	17·2	35·2	59·3	87·1	43·2	27·4	16·4	3·1

Zinc Rubidium Sulphate. $a = 3{\cdot}739$, $b = 1804$, $c = 845{,}640$.

Temp. ...	33·3°	41·2°	47·6°	55·6°	64·7°	77·5°	81·5°	70·2°	66·2°	55·3°	46·8°
Press. obs.	3·6	7·9	13·6	25·2	46·0	100·2	125·1	65·0	51·7	25·0	13·3
Press. calc.	4·0	7·7	13·7	24·9	45·9	100·2	125·8	65·5	51·2	24·4	12·9

Zinc Cæsium Sulphate. $a = 1{\cdot}733$, $b = 3135$, $c = 1{,}059{,}800$.

Temp.	34·4°	41·0°	46·7°	53·4°	59·8°	70·7°	60·8°	44·3°	34·4°
Press. obs. ...	5·9	9·3	15·0	25·2	38·4	76·4	41·1	12·7	5·4
Press. calc. ...	5·2	9·3	14·8	24·5	38·4	76·2	40·9	12·2	5·2

Zinc Ammonium Sulphate. $a = 5{\cdot}636$, $b = 471{\cdot}5$, $c = 622{,}000$.

Temp. ...	42·5°	47·6°	55·6°	59·7°	68·0°	70·2°	79·4°	64·7°	56·5°	45·0°	30·7°
Press. obs.	7·4	10·9	20·5	26·4	46·4	53·7	93·1	37·9	22·0	9·3	3·2
Press. calc.	7·6	11·3	20·5	27·4	46·8	53·8	92·7	37·8	21·8	9·3	2·8

Cadmium Rubidium Sulphate. $a = 4{\cdot}759$, $b = 471{\cdot}2$, $c = 449{,}370$.

Temp. ...	28·0°	34·6°	40·1°	45·4°	50·9°	56·4°	61·7°	67·5°	47·2°	37·9°	32·6°
Press obs.	23·1	35·0	47·8	63·9	85·1	111·8	142·5	184·5	69·6	42·6	31·2
Press. calc.	23·1	34·8	47·8	64·0	85·1	111·7	142·6	184·5	70·5	42·3	31·0

The corresponding potassium salt has not been obtained by us. Tutton (J., 1893, **63**, 407) and Wyrouboff (*Bull. Soc. franç. Min.*, **14**, 236) were unable to prepare it.

Cadmium Cæsium Sulphate. $a = 1{\cdot}245$, $b = 2735$, $c = 816{,}170$.

Temp.	25·7°	32·0°	34·5°	40·2°	46·1°	51·8°	61·0°	64·4°	48·4°	33·6°
Press. obs.	17·2	28·2	31·6	46·1	62·8	84·0	130·1	151·3	72·2	30·2
Press. calc.	17·9	27·4	32·0	45·2	62·8	84·6	130·7	151·4	71·5	30·3

Manganese Rubidium Sulphate. $a = -7{\cdot}084$, $b = 8419$, $c = 1{,}781{,}000$.

Temp.	27·5°	34·4°	41·0°	46·7°	53·4°	70·7°
Press. obs.	16·7	28·7	45·8	67·4	98·5	216·7
Press. calc.	16·3	28·6	46·3	67·3	98·5	216·8

As in the case of cadmium, the corresponding potassium salt does not appear to exist.

Manganese Cæsium Sulphate. $a = 2{\cdot}830$, $b = 2236$, $c = 830{,}860$.

Temp.	28·5°	36·4°	43·8°	51·7°	55·8°	65·4°
Press. obs.	13·9	23·9	39·7	69·8	88·3	152·3
Press. calc.	12·8	23·9	40·6	67·0	87·7	151·0

Ferrous Potassium Sulphate. $a = 6{\cdot}768$, $b = -866{\cdot}5$, $c = 244{,}400$.

Temp. ...	25·1°	32·5°	39·0°	45·0°	50·7°	55·7°	61·7°	71·5°	66·6°	51·2°	26·6°
Press. obs.	21·0	32·9	48·3	66·9	89·1	113·3	148·6	228·9	186·8	91·4	23·6
Press. calc.	21·7	33·7	48·6	66·8	88·9	113·5	148·3	229·6	186·6	91·2	23·8

Magnesium Potassium Sulphate. $a = 6{\cdot}863$, $b = -908{\cdot}3$, $c = 221{,}950$.

Temp.	50·8°	54·3°	60·3°	64·9°	70·4°	57·3°	44·9°	36·2°	27·7°
Press. obs. ...	87·6	103·9	138·6	171·2	217·1	120·4	64·3	40·2	24·5
Press. calc. ...	87·5	103·8	137·7	170·6	216·8	119·9	64·4	40·3	24·3

Magnesium Rubidium Sulphate. $a = 7{\cdot}752$, $b = -1148$, $c = 264{,}030$.

Temp.	31·4°	43·9°	66·9°	57·4°	46·3°	28·8°
Press. obs.	13·5	31·6	122·9	70·5	35·7	11·5
Press. calc.	13·5	31·4	122·5	71·9	36·8	11·2

Magnesium Cæsium Sulphate. $a = 6{\cdot}597$, $b = -751{\cdot}8$, $c = 260{,}600$.

Temp.	30·0°	36·6°	48·7°	57·1°	67·7°	53·2°
Press. obs.	18·9	28·1	55·1	84·8	139·4	69·0
Press. calc.	18·9	28·3	55·1	84·5	139·3	69·8

Magnesium Ammonium Sulphate. $a = 5{\cdot}383$, $b = 485{\cdot}1$, $c = 563{,}500$.

Temp.	42·8°	52·1°	61·2°	68·2°	43·7°	36·3°	28·4°
Press. obs. ...	18·2	35·2	61·2	92·8	19·7	11·5	6·3
Press. calc. ...	18·6	34·9	61·5	92·8	19·9	11·7	6·2

In the following table are given the first lower hydrate formed by each salt, the dissociation pressures, the heats of hydration, Q, per molecule of water vapour, and the affinities of the hydration processes, A, per molecule of liquid water; all at 50°.

Bivalent metal.	Univalent metal.	Hydrate.	Press. at 50°. mm.	Q_{50}. Calories.	A_{50}. Calories.
Cadmium	Rubidium	Dihydrate	81·5	10,500	81
	Cæsium	,,	77·5	10,600	104
Manganese	Rubidium	,,	81·2	13,000	82
	Cæsium	,,	61·5	13,300	260
Cobalt	Potassium	,,	41·2	14,000	520
	Cæsium	,,	24·0	14,400	860
	Rubidium	,,	23·0	14,300	890
	Ammonium	,,	18·5	14,800	1030
Zinc	Potassium	,,	37·2	13,800	580
	Cæsium	,,	19·1	15,500	1010
	Rubidium	,,	16·5	15,600	1103
	Ammonium	,,	13·6	15,400	1226
Nickel	Potassium	,,	21·2	14,100	940
	Cæsium	,,	14·0	13,400	1206
	Rubidium	,,	11·2	14,400	1350
	Ammonium	,,	7·0	15,400	1650
Ferrous	Potassium	Tetrahydrate	85·9	10,400	47·8
Magnesium	Potassium	,,	84·0	10,400	62·0
	Cæsium	,,*	59·0	10,800	287
	Rubidium	,,*	46·3	12,700	440
	Ammonium	,,*	30·5	13,700	710

* The tetrahydrate was not isolated in these cases.

Summary and Conclusion.

1. It has been shown that the double sulphates of the type $M''SO_4,M'_2SO_4,6H_2O$, on losing water, form dihydrates in all cases except those containing magnesium and ferrous iron, which form tetrahydrates.

2. In the case of the bivalent metals copper, cadmium, and manganese, which do not form heptahydrated sulphates, stable at the ordinary temperature, the order of the vapour pressures of the double salts formed with different alkali metals decreases with the alkali metals in the order K, Rb, Cs.

3. In the case of the bivalent metals cobalt, nickel, zinc, ferrous iron, and magnesium, which form heptahydrated sulphates, the order is K, Cs, Rb.

4. The dissociation pressures of the ammonium double salts in all cases examined lie near to and are always lower than the corresponding pressures of the rubidium salts.

The anomalous position of cæsium in the case of the double sulphates of those bivalent metals which form heptahydrated sulphates requires notice. The atomic diameters according to Bragg (*Phil. Mag.*, 1920, [vi], **40**, 169) of the univalent and bivalent metals, or otherwise the superficial area on which the electrons of

the outer shell are disposed, as well as the numbers of these electrons in the case of the bivalent metal, may be supposed to influence the stability of the molecule, and the relations of its parts. An examination of these data does not, however, lead to a definite conclusion regarding this anomaly. Moreover, since according to Sir J. J. Thomson ("The Electron in Chemistry," p. 68), the water molecule possesses electric moment, so that it may be attracted to the double salt molecule from the H or OH end, this property of water, in conjunction with the presence of katonic and anionic metals in the double salt, may possibly underlie the complex phenomena observed.

In conclusion, we desire to thank the Governors of the Royal Technical College, and the Carnegie Trust for the Universities of Scotland for the provision of scholarships which have enabled one of us (J. F.) to participate in this research.

THE ROYAL TECHNICAL COLLEGE,
GLASGOW. [*Received, March 4th,* 1924.]

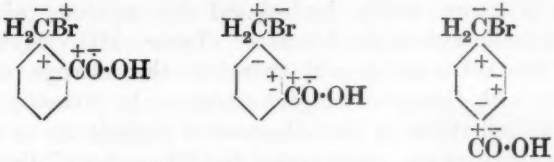
CLXIII.—*Polarity Effects in Aromatic Halogen Compounds.*

By JOHN BALDWIN SHOESMITH, ARTHUR CLEMENT HETHERINGTON, and ROBERT HENRY SLATER.

THE investigations of Lapworth and Shoesmith (J., 1922, **121**, 1392) and Shoesmith (J., 1923, **123**, 2828) have been continued and it has been found possible to predict differences in reactivity as regards hydrolysis and reduction by hydrogen iodide of the position isomerides of a number of halogen-substituted benzenoid compounds by a simple application of the principle of induced alternate polarities.

In addition to the induced alternate polarity influences in a molecule two other factors must be considered: (*a*) general polar influences, which are due to substituent atoms or groups and affect the molecule as a whole (Flürscheim, J., 1909, **95**, 718; Lapworth, *Mem. Manchester Phil. Soc.*, 1920, **64**, No. 3; Kermack and Robinson, J., 1922, **121**, 428; Lapworth and Shoesmith, *loc. cit.*; Robinson, *Ann. Reports*, 1922, 99), and (*b*) spatial and steric factors which operate generally in the aromatic series in the ortho-isomerides. When discussing differences in reactivity, it is therefore necessary to consider closely related compounds such as isomerides in order to eliminate (*a*) and meta- and para-isomerides to eliminate (*b*).

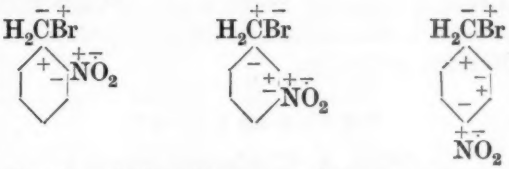
In the three isomeric ω-bromotoluic acids,



the bromine which has acquired an induced negative character is present in the meta-isomerides; thus the order of ease of hydrolysis should be $m>p$, and of reduction by hydrogen iodide, $p>m$, the reverse of that found in the methoxybenzyl bromides. Both these predictions were borne out by experiment (see Tables I and II).

Reduction of the carboxyl group under the conditions of the experiment is so small that it may be ignored.

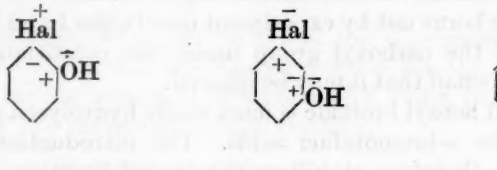
Unsubstituted benzyl bromide is more easily hydrolysed (Table I) than any of the ω-bromotoluic acids. The introduction of the carboxyl group therefore stabilises the benzyl bromide molecule as a whole, a condition even more pronounced in the case of the nitrobenzyl bromides, where the general polar influence (*a*) is very marked. The ease of hydrolysis of the latter compounds still follows the same rule, and the meta is the most readily hydrolysed isomeride (Table III).



The introduction of the nitro-group into a very reactive molecule such as *p*-methoxybenzyl bromide diminishes the reactivity of the latter to the order of that of the unsubstituted compound. It is thus seen that the restriction that differences in reactivity can be predicted only for very closely related compounds such as isomerides is necessary, otherwise 3-nitro-4-methoxybenzyl bromide (A) (which was the compound investigated) might be expected to be more reactive than the very reactive *p*-methoxybenzyl bromide (B) in virtue of the enhanced induced negative character of the bromine atom in the former. This induced effect is more than balanced by that of the strong general inhibiting influence of the nitro-group.

It has also been possible to show that 3-nitro-4-hydroxybenzyl bromide is more easily hydrolysed by aqueous alcohol than 3-nitro-4-methoxybenzyl bromide (Table III). Hydriodic acid reduces the nitro-group and therefore the change of order of reactivity with change of reagent could not be investigated.

The halogen atoms in the halogenated phenols are to be regarded as being situated one place nearer the " key-atom " than are those in the corresponding methoxybenzyl bromides. Thus the order of ease of reduction of such phenols should be, and actually is, *p* and *o*>*m*, the reverse of that already found in the latter series.



The order in which halogen atoms are removed from such compounds is *p*-iodo>*o*-iodo>*p*-bromo>*o*-bromo>*p*-chloro (Tables IV and V). The meta-isomerides show no tendency to reduce.* 4-Iodoresorcinol reduces far more rapidly than the iodophenols. It is, of course, recognised that in this series a quinonoid change could assist or addition of reducing agent might precede reduction, but the ultimate result is that which would be expected on the theory of induced alternate polarities.

EXPERIMENTAL.

[With A. C. HETHERINGTON.]

Bromotoluic Acids.—The ω-bromotoluoyl bromides from which the corresponding ω-bromotoluic acids were obtained were prepared by Davies and Perkin's method (J., 1922, **121**, 2202). The reactions are summarised as follows.

$$C_6H_4Me\cdot CO_2H \xrightarrow{SOCl_2} C_6H_4Me\cdot COCl \xrightarrow{Br} CH_2Br\cdot C_6H_4\cdot COBr \xrightarrow{HCO_2H} CH_2Br\cdot C_6H_4\cdot CO_2H.$$

ω-Bromo-*m*-toluoyl bromide has b. p. 160—165°/14 mm. and m. p. 23—25°. *ω-Bromo-*p*-toluoyl bromide* has b. p. 165—170°/12 mm. and m. p. 39—40° (Found : Br = 54·55. $C_8H_6OBr_2$ requires Br = 57·55 per cent. The low result is due to hydrolysis by atmospheric moisture).

* Franzen and Stäuble (*J. pr. Chem.*, 1921, [ii], **103**, 352) have prepared 3-chloro-α-naphthol from 2 : 3 : 4-trichloro-α-naphthol by reduction with hydriodic acid. The resulting monochloro-compound is quite stable to the reducing agent.

A mixture of 25 grams of the ω-bromotoluoyl bromide and 300 c.c. of 80 per cent. formic acid (*d* 1·2) was warmed at 30—35° for 1 hour and poured into water, and the precipitated acid was dried and crystallised from benzene. The m. p.'s of the acids are, *o*- 146°, *m*- 150°, and *p*- 223° (compare Zalkind, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 508; Zalkind and Semenov, *ibid.*, p. 512).

Hydrolysis of the ω-Bromotoluic Acids.—Approximately 0·10 gram of the acid was dissolved in 20 c.c. of absolute alcohol, 5 c.c. of water were added, and the volume was made up to 25 c.c. with alcohol. The solution was heated at 76° (vapour of boiling carbon tetrachloride) for 5 minutes longer than the time recorded, the extra time being that necessary for equilibration of temperature, and the total acidity (hydrogen bromide + organic acid) determined by titration with *N*/10-alkali and methyl-red. A correction was applied for the organic acid.

The results are summarised in Table I. t = time from commencement of experiment in hours. w = weight of compound used in grams. x = percentage changed.

TABLE I.

	o-Compound.		*m*-Compound.		*p*-Compound.		Benzyl bromide.	
t.	*w*.	*x*.	*w*.	*x*.	*w*.	*x*.	*w*.	*x*.
½	0·1068	5·0	0·1019	27	0·1076	13	0·0804	57
1	0·1158	7·0	0·1010	42	0·1049	30	,,	81
2	0·1031	4·9	0·1207	70	0·1126	54	,,	92
4	0·1089	4·7	0·1001	87	0·1110	74	,,	96
8	0·1126	4·8	0·1149	90	0·1032	83	,,	97
16	—	—	0·1154	94	0·1207	90	0·0975	99
32	—	—	0·1199	98	0·0998	94	—	—

In the case of ω-bromo-*o*-toluic acid, x denotes, not the percentage of acid hydrolysed, but that calculated from the excess titration over the quantity required for neutralisation of the carboxyl group. The fall from the maximum is due to the following changes :

$$C_6H_4\!<\!\begin{matrix}CH_2Br\\CO_2H\end{matrix} \rightleftharpoons C_6H_4\!<\!\begin{matrix}CH_2\\CO\end{matrix}\!>\!O \rightleftharpoons C_6H_4\!<\!\begin{matrix}CH_2\cdot OH\\CO_2H\end{matrix}$$

(I.) (II.) (III.)

The hydrolysis of ω-bromo-*o*-toluic acid (I) to ω-hydroxy-*o*-toluic acid (III) is accompanied by the formation of hydrobromic acid and phthalide (II). In the titrations, which estimate both the halogen acid and the carboxylic acid, the values fall until equilibrium is reached in the production of phthalide. This is due to the spatial influences classified under heading (*b*).

Reduction of the Isomeric ω-Bromotoluic Acids at 110° *by Hydriodic*

Acid.—Approximately 0·10 gram of the acid, dissolved in 15 c.c. of glacial acetic acid, was heated with 10 c.c. of constant-boiling hydriodic acid in the vapour of boiling toluene. After a definite interval the liberated iodine was titrated with thiosulphate. A blank experiment to ascertain the amount of air oxidation was carried out on each occasion.

The results are summarised in Table II; t, w, and x have the same significance as before.

TABLE II.

	o-Compound.		*m*-Compound.		*p*-Compound.		Benzyl bromide.	
t.	*w*.	*x*.	*w*.	*x*.	*w*.	*x*.	*w*.	*x*.
1½	0·1026	11	0·1010	24	0·1044	49	0·1518	34
3	0·1223	24	0·1003	43	0·1033	73	0·1549	55
6	0·1161	42	0·1001	68	0·1001	91	0·0900	78
12	0·0931	51	0·1066	86	0·0901	99	0·1103	92

The behaviour of the *o*-compound is again abnormal owing to phthalide formation.

Reduction of the isomeric toluic acids for 6 hours under the same conditions as those in the previous experiment takes place to the following extents : *o*- 0·16, *m*- 0·49, *p*- 0·43 per cent.

Corrections for such small quantities have not been applied to the bromo-acid reduction figures.

o-*Nitrobenzyl Bromide.*—*o*-Nitrobenzyl chloride (Haeussermann and Beck, *Ber.*, 1892, **25**, 2445) (1 part) was boiled with concentrated aqueous sodium acetate (2 parts) and the *o*-nitrobenzyl acetate converted into *o*-nitrobenzyl alcohol by boiling 50 per cent. sulphuric acid. This alcohol was crystallised from hot water and, when mixed with the calculated quantity of phosphorus pentabromide, readily gave o-*nitrobenzyl bromide*, light yellow plates, m. p. 45·5°, from light petroleum (Found : Br = 36·82. $C_7H_6O_2NBr$ requires Br = 37·00 per cent.).

m-Nitrobenzyl bromide was prepared from *m*-nitrobenzyl alcohol and hydrogen bromide in dry benzene, two layers forming. The crystals that separated from the lower layer and the further quantity obtained by evaporating the benzene were recrystallised from light petroleum ; the product had m. p. 57°.

p-Nitrobenzyl bromide, prepared by Lyons and Reid's method (*J. Amer. Chem. Soc.*, 1917, **39**, 1729) and recrystallised several times from light petroleum to remove benzal bromide, melted at 98·5°.

3-*Nitro*-4-*hydroxybenzyl bromide* was obtained from the corresponding alcohol, which was prepared by Stoermer and Behn's method (*Ber.*, 1901, **34**, 2459). The alcohol crystallised from water in bright yellow needles, m. p. 97°. A solution of these in the

minimum of dry benzene was saturated with dry hydrogen bromide, the benzene evaporated, and the residue crystallised from light petroleum, 3-*nitro*-4-*hydroxybenzyl bromide* being obtained in yellow prismatic needles, m. p. 82° (Found : Br = 34·46. $C_7H_6O_3NBr$ requires Br = 34·44 per cent.).

3-*Nitro*-4-*methoxybenzyl bromide*, prepared by methylating 3-nitro-4-hydroxybenzyl alcohol with methyl iodide and potassium hydroxide, recrystallising the product from hot water, and converting it (m. p. 69°) into the bromide as above, crystallised from light petroleum in pale yellow needles, m. p. 108° (Found : Br = 32·84. $C_8H_8O_3NBr$ requires Br = 32·49 per cent.).

These bromides were hydrolysed under the same conditions as the ω-bromotoluic acids. The hydrobromic acid liberated was titrated with *N*/10-caustic alkali as before, except in the case of 3-nitro-4-hydroxybenzyl bromide, where *N*/20-ammonium hydroxide was used and any hydrolysis of the unchanged bromide during the titration avoided.

The results are summarised in Table III.

TABLE III.

	Nitrobenzyl bromides						3-Nitro-4-methoxybenzyl bromide.	
	Ortho.		Meta.		Para.			
t.	*w*.	*x*.	*w*.	*x*.	*w*.	*x*.	*w*.	*x*.
½	0·1267	10·8	0·1226	12·0	0·1168	11·0	0·1067	73·2
1	0·1190	19·2	0·1037	23·0	0·1045	19·5	0·1008	90·2
2	0·1022	32·4	0·1083	38·4	0·1147	32·8	0·1023	95·5
4	0·1010	54·7	0·1171	59·3	0·1015	54·6	0·1116	97·1
8	0·1081	78·9	0·1196	85·1	0·1146	78·9	0·1037	98·7
16	0·1040	93·9	0·1194	96·2	0·1068	95·3	0·1038	99·3
32	0·0998	99·1	0·1176	99·8	0·1041	99·5	0·1039	99·8

3-Nitro-4-hydroxybenzyl bromide.

t	¼	½	1	2
w	0·1008	0·1024	0·1031	0·1028
x	85	96	99	100

[With ROBERT HENRY SLATER.]

The *o*- and *p*-halogenated phenols were prepared from the corresponding aminophenols by the usual methods.

m-Chlorophenol was most conveniently obtained from *m*-chloronitrobenzene, 100 grams of which at 50° were dropped into a mechanically stirred mixture of 200 grams of iron filings, 400 c.c. of water, and 15 c.c. of concentrated hydrochloric acid (compare Morgan, J., 1900, **77**, 1204), the heat of reaction, after slight preliminary warming, maintaining the temperature at 95°. After an hour's heating at 90°, the whole was cooled, neutralised with 30 grams of sodium bicarbonate, and the chloroaniline distilled

in steam and obtained in 50 per cent. yield from the dried, ethereal extract of the distillate. Its solution was diazotised (Varnholt, *J. pr. Chem.*, 1887, **36**, 27), heated, filtered, and the chlorophenol extracted with ether and purified by distillation.

m-Bromophenol, prepared in a similar manner from *m*-bromonitrobenzene [bromination of nitrobenzene (Wheeler and McFarland, *Amer. Chem. J.*, 1897, **19**, 366) is much more satisfactory than chlorination], distils at 125—127°/12 mm. (Diels and Bunzl, *Ber.*, 1905, **38**, 1495, give b. p. 135—140°/12 mm.).

m-Iodophenol was obtained from *m*-nitroaniline (Nölting and Stricker, *Ber.*, 1887, **20**, 3020), the intermediate *m*-iodonitrobenzene being reduced with iron and hydrochloric acid.

4-Iodoresorcinol was prepared by Stenhouse's method (*Annalen*, 1874, **171**, 311). The compulsory use of 220 grams of litharge to iodinate 20 grams of resorcinol prevents reduction of the iodoresorcinol by the hydriodic acid produced in the reaction.

Reduction of the Halogenated Phenols.—Approximately 0·6 gram of the phenol was made up to 2·5 c.c. with glacial acetic acid in a 5 c.c. stoppered measuring cylinder, 2·5 c.c. of glacial acetic acid containing 0·410 gram of hydrogen iodide per c.c. (Lapworth and Shoesmith, *loc. cit.*) were added, and the whole was well mixed and placed in a thermostat at 25°. One c.c. portions were withdrawn at definite intervals and the liberated iodine was estimated with thiosulphate. A comparison of the ease of reduction of *o*-iodophenol, *p*-iodophenol and *p*-bromophenol was thus obtained. The results are summarised in Table IV.

This method did not furnish a satisfactory reduction curve for *o*-bromophenol, but the above results having been obtained for the iodophenols and *p*-bromophenol at 25° a series of experiments at 78° completed the comparison: 10 c.c. of a standard solution of the halogenated phenol in glacial acetic acid and 10 c.c. of constant-boiling hydriodic acid were heated together in the vapour of boiling alcohol; the liberated iodine was estimated as before. The results are summarised in Table V.

In Tables IV and V, x has the same significance as before, and t is the time in minutes from the commencement of the experiment. In Table IV, w is the total weight of the phenol used, whilst in Table V it represents the weight used in each reduction.

p-Chlorophenol was the only one of the chloro-isomerides to show any reduction under the different conditions described, and this was very slight. A solution of the phenol in glacial acetic acid containing 0·37 gram of hydrogen iodide per c.c. showed a reduction of about 10 per cent. after 4 hours. Complete reduction was never observed.

TABLE IV.

	o-Iodophenol. w = 0·6104 gm.	*p*-Iodophenol. w = 0·6394 gm.	*p*-Bromophenol. w = 0·6070 gm.
t.	*x.*	*x.*	*x.*
15	28·2	69·0	4·4
45	56·2	88·8	8·7
105	75·6	95·4	15·9
225	90·0	100·0	28·7

TABLE V.

	o-Bromophenol. w = 0·1730 gm.	*p*-Bromophenol. w = 0·1719 gm.
t.	*x.*	*x.*
60	18·7	40·7
120	31·7	68·4
180	39·6	83·9
240	47·6	94·2
300	53·0	100·0

The meta-halogenated phenols did not reduce in any circumstances.

4-Iodoresorcinol was completely reduced in ½ hour at 25° in glacial acetic acid solution containing 0·40 gram of hydrogen iodide per c.c.

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EDINBURGH UNIVERSITY. [*Received, November 23rd,* 1923. *Revised, March 3rd,* 1924.]

CLXIV.—*The Correlation of Additive Reactions with Tautomeric Change. Part III. The Cyano-imino Additive Process.*

By EDITH HILDA INGOLD.

THE view has been expressed (Usherwood, J., 1923, **123**, 1717) that the fundamental reactions on which all types of tautomeric phenomena depend are reversible additive processes, tautomerism representing the particular case in which the two residues required for the addition are present in the same molecule, either adjacent to one another, as in triad systems, or in non-adjacent positions, as in ring-chain tautomeric systems. The study of these reversible additions is therefore of the utmost importance for the proper understanding of the derived tautomeric changes, and this paper extends the work recorded in the previous parts of the series to the intermolecular prototype of the imino-ename system, $>C[H]\cdot\dot{C}{:}NH \rightleftharpoons >C{:}\dot{C}\cdot NH[H]$.

The cyano-imino additive reaction, $\geqslant C[H] + \cdot C{:}N \longrightarrow \geqslant C\cdot\dot{C}{:}N[H]$, has been extensively studied, particularly by Thorpe and his collaborators, but, so far as the author is aware, the complementary degradation, $>C\cdot\dot{C}{:}N[H] \longrightarrow \geqslant C[H] + \cdot C{:}N$, and the

consequent equilibria have not previously been investigated. It is shown below that such degradation actually occurs, and, moreover, that it takes place under the same experimental conditions as those in which the imino-compound itself is formed.*

The examples studied were β-imino-α-cyano-α-phenyl-β-*o*-tolylethane (I), which readily undergoes fission into phenylacetonitrile and *o*-toluonitrile, and ethyl β-imino-α-cyano-β-phenylpropionate (II), which similarly undergoes degradation to ethyl cyanoacetate and benzonitrile.

(I.) $C_7H_7{\cdot}C(:N[H]){\cdot}CHPh{\cdot}CN \longrightarrow CH[H]Ph{\cdot}CN + C_7H_7{\cdot}CN.$

(II.) $C_6H_5{\cdot}C(:N[H]){\cdot}CH(CN){\cdot}CO_2Et \longrightarrow CH[H](CN){\cdot}CO_2Et + C_6H_5{\cdot}CN.$

In each case a balanced action results.

Experiments were also undertaken to detect the equilibria between ethyl cyanoacetate and ethyl cyanoiminoglutarate (III),

$$2CH_2(CN){\cdot}CO_2Et \rightleftharpoons CO_2Et{\cdot}CH_2{\cdot}C(:NH){\cdot}CH(CN){\cdot}CO_2Et \quad \text{(III.)}$$
$$\longrightarrow CH_3{\cdot}C(:NH){\cdot}CH(CN){\cdot}CO_2Et \quad \text{(IV.)}.$$

The formation of (III) is, however, only the first stage of a series of reactions leading to (IV), and experiments on the equilibration were therefore abandoned.

Experimental.

Degradation of β-Imino-α-cyano-α-phenyl-β-o-tolylethane.—A mixture of the imino-compound (Atkinson, Ingham, and Thorpe, J., 1907, **91**, 588) (8·6 grams) and alcoholic sodium ethoxide (0·83 gram of sodium and 10·1 grams of ethyl alcohol) was heated on the steam-bath for 12·5 hours, water was added, and the oil which separated extracted with ether. The ethereal solution was washed with water and thoroughly shaken with hydrochloric acid (3 : 1), and with dilute aqueous sodium carbonate, the solvent was evaporated, and the residue distilled in steam. The ethereal extract of the colourless oil in the distillate was dried and evaporated, and the residue distilled under 20 mm., three fractions being obtained, b. p. 200—225° (about 0·5 gram), 225—227° (about 2 grams), and 227—231° (about 0·5 gram) (Found: for the main fraction, C = 81·8; H = 6·0. Calc. for C_8H_7N, C = 82·0; H = 6·0 per cent.). This oil was a mixture of phenylacetonitrile and *o*-toluonitrile, for on hydrolysis with four times its weight of boiling 75 per cent. sulphuric acid it yielded a mixture of *o*-toluic acid, m. p. 104° (Found:

* E. von Meyer has, however, observed (*J. pr. Chem.*, 1888, [ii], **38**, 339) that "bimolecular propionitrile" yields the monomeric nitrile when fused with sodium, or on pyrogenic decomposition. The latter reaction closely resembles the pyrogenic degradation of the aldols.

C = 70·4; H = 5·8. Calc., C = 70·6; H = 5·9 per cent.), which was precipitated by water, and phenylacetic acid (Found: C = 70·3; H = 5·8. Calc., C = 70·6; H = 5·9 per cent.), which was extracted with ether and identified by the mixed melting point method.

The hydrochloric acid extract from the original ethereal solution, when diluted slightly, gave an oil, insoluble in ether, which solidified (about 0·5 gram) after treatment with sodium carbonate solution, and was identified as cyanbenzyline, m. p. 104—107°, after crystallisation from alcohol (Found: C = 81·9; H = 6·0. Calc., C = 82·0; H = 6·0 per cent.).

The residue after removal of the phenylacetonitrile and toluonitrile by steam distillation was extracted with ether, and from the dried extract about 1·8 grams of unchanged imino-compound, b. p. 255—260°/14 mm. (Found: C = 81·7; H = 6·1. Calc., C = 82·0; H = 6·0 per cent.), were isolated.

Degradation of Ethyl β-Imino-α-cyano-β-phenylpropionate.—This decomposition was effected as in the preceding case (11·8 grams of the imino-compound [Atkinson, Ingham, and Thorpe, *loc. cit.*], 1·24 grams of sodium, 16 grams of alcohol; period of heating, 10 hours). The solution was diluted with water, strongly acidified with hydrochloric acid, and extracted with ether. The solid (A), m. p. 120—124°, that separated from the wet extract on concentration was washed with ether, the washings and the remainder of the ethereal solution were evaporated, and the residue distilled in steam. The non-volatile portion, which crystallised on cooling, was identical with (A) (total weight 6·2 grams); after several crystallisations from alcohol and from ether, it melted at 123—125° and was identified as unchanged imino-compound by a mixed melting-point determination (Found: C = 67·0; H = 5·3. Calc., C = 66·7; H = 5·6 per cent.).

The steam distillate was extracted with ether, the ethereal solution dried and evaporated, and the residual oil (about 2·5 grams) distilled in a vacuum. On redistilling at the ordinary pressure, the main fraction passed over at 186—188°, and was identified as benzonitrile by hydrolysis to benzoic acid.

The steam distillate, after extraction with ether, was neutralised and evaporated to dryness. The solid residue (11·8 grams) was heated on a steam-bath for 2 hours with 25 c.c. of sulphuric acid and 31 c.c. of alcohol, and the mixture poured into water and extracted with ether. Ethyl malonate (2·7 grams), b. p. 196—198°, was isolated from the extract and converted into malonamide, the identity of which was established in the usual way (Found: C = 35·2; H = 5·7. Calc., C = 35·3; H = 5·6 per cent.).

Action of Sodium Ethoxide on Ethyl β-Imino-α-cyanoglutarate: Alcoholysis to Ethyl β-Imino-α-cyanobutyrate.—The reaction was carried out as in the other two cases (22·4 grams of imino-compound [Best and Thorpe, J., 1909, **95**, 1518], 2·3 grams of sodium, 36 c.c. of alcohol; period of heating, 2 hours), water was added, and the solution faintly acidified with acetic acid and distilled in steam until the distillate ceased to give an acid reaction. The solid (13·5 grams) which separated in the distilling flask was recognised as ethyl β-imino-α-cyanobutyrate. Extraction of the aqueous residue with ether yielded 1·5 grams of the unchanged imino-cyanoglutarate, so that 95 per cent. of the material was accounted for.

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IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON. [*Received, March 21st*, 1924.]

CLXV.—*The Chemistry of Posidonia Fibre. Part II. The Cellulose.*

By JOHN CAMPBELL EARL.

ALTHOUGH it possesses many of the features of a land plant, *Posidonia australis* has its habitat in the shallow sea waters on certain sheltered parts of the Australian coast. It might be expected, therefore, that it would build up as its chief structural material a cellulose differing from the celluloses of land plants growing under normal land conditions. Data have now been obtained which enable posidonia cellulose to be compared with cotton cellulose.

The cellulose was isolated from posidonia fibre by the usual chlorination method, any remaining non-cellulose constituents being removed with hot 2 per cent. sulphuric acid (J., 1923, **123**, 3223). The cellulose was degraded by Irvine and Hirst's method (J., 1922, **121**, 1585), the first stage being the formation of cellulose triacetate. Allowance being made on 10 grams of air-dried cellulose for 0·32 gram of fibre not entirely disintegrated by the chlorination treatment, from which the chloroform solution of the triacetate was filtered before evaporation, 9·68 grams of posidonia cellulose gave 15·39 grams of the triacetate (Irvine and Hirst obtained 16·61 grams from 10 grams of air-dried cotton cellulose).

Since direct distillation with 10 per cent. sulphuric acid gave no trace of volatile acid, the acetate (about 0·3 gram) was boiled with 25 c.c. of *N*/2-caustic soda for 2 hours, 150 c.c. of 10 per cent.

sulphuric acid were added, the mixture was distilled with steam, and the acetic acid in the distillate titrated with standard alkali (Found : $CH_3 \cdot CO = 44{\cdot}3$, $45{\cdot}0$. Calc., $CH_3 \cdot CO = 44{\cdot}8$ per cent.).

Posidonia cellulose triacetate gave $[\alpha]_D - 39{\cdot}8°$ in chloroform ($c = 0{\cdot}7352$); for cotton cellulose triacetate Irvine and Hirst (*loc. cit.*) found $[\alpha]_D - 22{\cdot}3°$ ($c = 0{\cdot}8092$).

The conversion of the triacetate into the constituent monosaccharides was effected by Irvine and Hirst's method; the results are compared with those of one of their experiments on cotton cellulose.

	Posidonia.	Cotton.
Grams of cellulose triacetate	4·9	3·99
C.c. of acid methyl alcohol	60	60
% concentration of HCl.....	0·79	0·75
Time (hours) of digestion at 125°	63	65
Gram of residue undissolved	0·09	0·012
Grams of mixed glucosides	2·56	2·56
$[\alpha]_D$ of mixed glucosides in methyl alcohol ...	+89°	+92°

On neutralising and evaporating the methyl-alcoholic solution, crystals (0·75 gram) separated which had $[\alpha]_D + 144°$ in water, but after recrystallisation from ethyl alcohol showed $[\alpha]_D^{22°} + 156°$ in water ($c = 1{\cdot}194$) and m. p. 168° (corr.). The mother-liquors on evaporation yielded a syrup (1·87 grams; $[\alpha]_D + 62°$ in acid methyl alcohol) which, on prolonged digestion with acid methyl alcohol (0·79 per cent.) at 100°, gave $[\alpha]_D + 106°$, *i.e.*, the value for an equilibrated mixture of α- and β-methylglucosides. From the equilibrated solution a sample of pure α-methylglucoside was isolated having $[\alpha]_D + 158°$ in water ($c = 1{\cdot}180$) and m. p. 168° (corr.).

The results of the experiments show that more than 95 per cent. of the posidonia cellulose triacetate is converted into a mixture of α- and β-methylglucosides. In view of the fact that the yield of triacetate from the cellulose is practically quantitative, it may be concluded that posidonia cellulose, like cotton cellulose, is of the poly-anhydroglucose type. The very great difference in optical rotation of the triacetates from the two celluloses no doubt indicates a difference in their chemical structure. The nature of this difference could probably be elucidated by an examination of the partial degradation products of posidonia cellulose, and it is understood that work on these lines is now being undertaken by Principal Irvine and his collaborators.

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THE UNIVERSITY OF SYDNEY. [*Received, March 19th*, 1924.]

CLXVI.—*Tautomerism of the Mesoxalic Acid and Pyruvic Acid Phenylhydrazones. Evidence for the Hydrazone Structure of the Tautomerides.*

By HAROLD ROBERTS STEVENS and FRED WILBERT WARD.

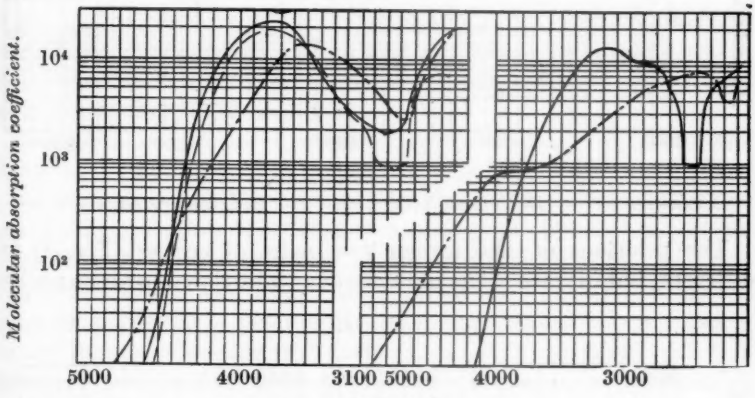
THE methods hitherto employed in elucidating the structure of the so-called phenylhydrazones of mesoxalic and pyruvic acids are open to certain objections which make a fresh investigation on spectroscopic lines of value. The existing arguments of greatest weight are derived from Pechmann's preparation of glyoxylic ester acetylphenylhydrazone, by the action of acetic anhydride, from the compound for which the formula $NHPh{\cdot}N{:}C(CO_2H){\cdot}CO_2Et$ or $NPh{:}N{\cdot}CH(CO_2H){\cdot}CO_2Et$ is possible, and from Dimroth's work on the condensation products of benzenediazonium chloride and tribenzoylmethane (*Ber.*, 1908, **41**, 4012). Dimroth showed that of the two compounds $CBz_3{\cdot}N{:}NPh$ and $CBz_2{:}N{\cdot}NBzPh$, both of which can be isolated, the hydrazone is the stable form. This may be due to the three benzoyl groups being attached to one carbon atom in the azo-compound, causing a peculiar instability, but there is no valid ground for inferring from this the instability of azo-compounds in general in comparison with the isomeric hydrazones. Pechmann's work is vitiated by the ease with which, as Dimroth showed, the acyl group can migrate even in indifferent solvents.

We proposed to compare the absorption spectra of the parent substance and its methyl derivatives, *e.g.* $NPhMe{\cdot}N{:}C(CO_2H)_2$ and $NPh{:}N{\cdot}CMe(CO_2H)_2$, but being unable to prepare any derivative of benzeneazomethylmalonic acid, and having reason to suppose that the replacement of the carboxyl group by hydrogen at the end of the side chains of such compounds as these malonic acid derivatives would not seriously alter the *type* of absorption curve (Ward, *Biochem. J.*, 1923, **17**, 895), we used benzeneazoethane instead of the inaccessible benzeneazomethylmalonic acid as the standard azo-compound in our comparison.

The result leaves the issue in doubt. The curves for the " phenylhydrazones " of mesoxalamide and mesoxalic acid (Fig. 1) show the close resemblance one expects in compounds differing so little in constitution, but are different from either of the standards. They show each a maximum, at 3550 Å. and 2650 Å., respectively, whereas there are two maxima and two minima, at 2700 Å. and 3900 Å., and 2350° Å. and 3400 Å. respectively, in the curve of benzeneazoethane (Fig. 3). Mesoxalamide phenylmethylhydrazone gives yellower solutions than the parent substance, although in the solid state it is almost colourless, and its absorption curve is much more flattened.

In the case of the "phenylhydrazone" and phenylmethylhydrazone of pyruvic acid (Fig. 2), all trace of resemblance disappears. The curve of the "phenylhydrazone" is very like those of the two "phenylhydrazones" already examined, although shifted approximately 350 Å. toward the ultra-violet; that of its methyl derivative shows no resemblance to this "phenylhydrazone" or "tautomeride" type and very little to the curve of the other phenylmethylhydrazone; both solid and solution are yellow, the absorption is much more general, and a second slight maximum appears in the curve.

FIG. 1. FIG. 2.



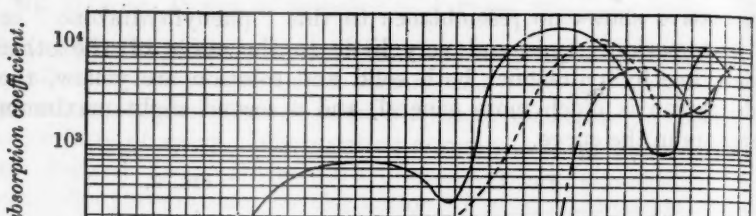
Mesoxalamide phenylhydrazone ——
" phenylmethylhydrazone – – – –
Mesoxalic acid phenylhydrazone – – –

Pyruvic acid phenylhydrazone ——
" " phenylmethylhydrazone – – – –

It is possible, although not probable on the evidence of the curves, that the "phenylhydrazones" are mixtures of both forms in solution. A more probable explanation of the dissimilarity is that for some reason the curves of these phenylmethylhydrazones are not typical of the hydrazone structure. In order, then, to furnish definite evidence of the structure of the "phenylhydrazones," it was necessary to demonstrate this abnormality by a comparison of other pairs of phenyl- and phenylmethyl-hydrazones, and to establish the hydrazone and azo typical curves on a more general basis. Baly and Tuck (J., 1906, **89**, 982) have shown the close similarity of the absorption curves of the phenylhydrazone and phenylmethylhydrazone of acetaldehyde and also of the corresponding benzaldehyde derivatives. We have repeated this work using the more modern method, in order to obtain curves comparable with those of the

other substances we have examined and, as additional examples of azo curves, have plotted those of azobenzene and benzeneazoformamide, $NPh{:}N{\cdot}CO{\cdot}NH_2$.

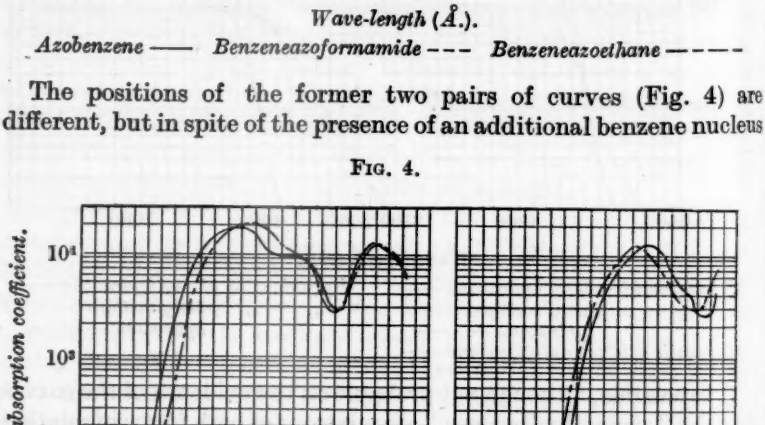
FIG 3.



Azobenzene —— *Benzeneazoformamide* - - - *Benzeneazoethane* – – – –

The positions of the former two pairs of curves (Fig. 4) are different, but in spite of the presence of an additional benzene nucleus

FIG. 4.



Benzaldehydephenylhydrazone —— *Acetaldehydephenylhydrazone* ——
„ *phenylmethyl-hydrazone* – – – – „ *phenylmethyl-hydrazone* – – – –

in the second case, the type is undoubtedly the same. With equal ease it is possible to see the azo type in the three azo curves (Fig. 3). Although the data are insufficient for any generalisation,

a comparison of the curves of the hydrazone with that of the corresponding azo-compound suggests that the difference consists in the disappearance from the azo curve of one of the two bands. The parts of the curves of acetaldehydephenylhydrazone and benzeneazoethane that lie between 2100 Å. and 3300 Å. are almost identical; above 3300 Å. there is nothing in the hydrazone curve corresponding to the maximum in the azo curve. The curves of azobenzene and benzaldehydephenylhydrazone show a similar relation, though these are not exactly corresponding compounds.

In our opinion, a comparison of the three types, the tautomeride type, the hydrazone type, and the azo type, leaves no doubt that the tautomeride type is the same as the hydrazone type; the curves of the "phenylhydrazones" of mesoxalic and pyruvic acids have none of the characteristics of the azo curves examined and bear a strong likeness to those of the phenylhydrazones. These compounds are in truth phenylhydrazones.

There remains for consideration the evident abnormality of the phenylmethylhydrazones of pyruvic acid and mesoxalamide (Figs. 1 and 2). It would be irrevelant to the subject of this paper to consider the question in detail, and it suffices to offer the suggestion, which it is hoped to examine by further investigation, that the replacement of the α-hydrogen in the phenylhydrazones by a methyl group increases the basicity of the α-nitrogen sufficiently to cause a certain amount of internal salt formation. It is consistent with this that those compounds examined which do not possess a salt-forming group do not give rise to abnormal absorption curves.

EXPERIMENTAL.

Mesoxalic acid was prepared from dibromomalonic acid (Conrad and Reinbach, *Ber.*, 1904, **35**, 1819) and the phenylhydrazone by Fischer's method (*Ber.*, 1884, **17**, 378). The phenylmethylhydrazone could not be prepared.

Mesoxalamide phenylhydrazone was prepared from dibromomalonamide and phenylhydrazine (Ruhemann and Orton, J., 1895, **67**, 1002), and also from mesoxalamide and phenylhydrazine hydrochloride. The corresponding phenylmethylhydrazone, prepared by mixing warm aqueous solutions of phenylmethylhydrazine sulphate and mesoxalamide, formed pale yellow crystals, m. p. 229°, from alcohol (Found: C = 54·5; H = 5·5; N = 9·9. $C_{10}H_{12}O_2N_4$ requires C = 54·5; H = 5·45; N = 10·1 per cent.). Mesoxalamide was prepared by the action of 0·88 ammonia on dihydroxymalonic ester, itself made as described by Curtiss (*J. Amer. Chem. Soc.*, 1911, **33**, 63) and Lemaire (*Rec. trav. chim.*, 1910, **29**, 24).

The phenyl- and phenylmethyl-hydrazones of pyruvic acid were

prepared by adding the free bases in alcohol to alcoholic solutions of the acid; in the second case, a crystalline precipitate was obtained immediately instead of oily drops, and the m. p. was 80° (sharp) instead of 76—78° (compare E. Fischer, *Ber.*, 1883, **16**, 2241). The corresponding derivatives of benzaldehyde were prepared similarly.

Acetaldehydephenylhydrazone (Stobbe, *Ber.*, 1913, **46**, 2887) was recrystallised three times from ligroin and dried in a vacuum over paraffin wax. The phenylmethylhydrazone, which is mentioned but not described by Baly and Tuck (*loc. cit.*), was prepared by adding phenylmethylhydrazine to an excess of aldehyde dissolved in light petroleum, evaporating off the solvent and excess aldehyde, and extracting with ether; after drying over potassium carbonate, the extract was thrice distilled in a vacuum. It is a colourless oil, b. p. 136°/25 mm., with a peculiar odour (Found: C = 73·2; H = 8·1. Calc. for $C_9H_{12}N_2$, C = 73·0; H = 8·1 per cent.).

Benzeneazoethane was prepared by Fischer's method (*Annalen*, 1879, **199**, 328). The pale yellow oil was distilled twice in a vacuum.

Benzeneazoformamide was prepared by the oxidation of phenylsemicarbazide with hot acid potassium permanganate (Widman, *Ber.*, 1893, **26**, 2612).

Spectroscopy.—The apparatus used was a Hilger quartz ultraviolet spectrophotometer, and the method that commonly employed with this instrument; it is described by one of us (Ward, *Biochem. J.*, 1923, **17**, 891).

The absorption curves are plotted with the wave-lengths on an arithmetic scale and the molecular absorption coefficients on a logarithmic. The molecular absorption coefficient is calculated from the equation $M = \frac{1}{d} \cdot \frac{\log I_0 - \log I}{C}$, where d = thickness of the layer in cm. and C = molecular concentration.

The solutions of the phenylhydrazones of acetaldehyde and benzaldehyde were used as soon as possible to avoid the change of colour produced by standing, either in solution or in the solid state.

The authors' thanks are due to Dr. W. H. Mills, F.R.S, at whose suggestion this research was undertaken. One of them (H. R. S.) thanks the Advisory Council of the Department for Scientific and Industrial Research also for a grant which has enabled him to take part in this investigation.

THE UNIVERSITY, CAMBRIDGE. [*Received, February 23rd*, 1924.]

NOTE by H. R. S.—The interaction of phenylhydrazine and bromoethyl- or bromomethyl-malonic ester, followed by treatment with ammonia, with or without a preliminary oxidation with mercuric

oxide, gave in several cases a 25 per cent. yield of mesoxalamide phenylhydrazone; this is under investigation.

For the purpose of testing a theory about the course of this reaction, the interaction of ethylidenemalonic ester and phenylhydrazine was studied. On mixing the two liquids, heat was liberated but no solid deposited. The liquid was poured into 20 per cent. hydrochloric acid and the oil extracted with ether. From the acid solution, on standing, a large crop of white crystals was deposited, which, recrystallised from 5 per cent. hydrochloric acid, melted at 130° (Found : C = 55·0; H = 6·97. The additive product $NHPh{\cdot}NH{\cdot}CHMe{\cdot}CH(CO_2Et)_2,HCl$ requires C = 54·7; H = 7·16 per cent.). Addition of this solid to water causes the deposition of an oil which is presumably the free base (compare Blank, *Ber.*, 1893, **26**, 145).

Two new phenylhydrazones were prepared, the *s-trichlorophenylhydrazones* of ethyl mesoxalate and of mesoxalic acid, slightly yellow solids, m. p. 75° and 170°, respectively.

We also prepared bromomethyl- and bromoethyl-malonamides. The method by which Nef prepared chloromethylmalonamide (*Annalen*, 1881, **209**, 23) is not convenient in these cases, but almost quantitative yields were obtained by evaporating a warm glacial acetic acid solution, containing the ethyl- or methyl-malonamide and the calculated quantity of bromine, to dryness in a vacuum over sodium hydroxide; the residue was washed with ether and recrystallised from water or alcohol. A more rapid method (yield 70 per cent.) consists in adding *excess* of bromine gradually to a solution of the alkylamide in hot water. The solution is cooled and the product filtered off and recrystallised. If an excess of bromine (about 30 per cent.) is not used, unbrominated alkylmalonamide remains as impurity and is concentrated by recrystallisation.

Both substances are white solids that crystallise well from alcohol and from water. The *methyl* compound, $CMeBr(CO{\cdot}NH_2)_2$, melts at 172° (Found : Br = 40·6. Theo., Br = 41·1 per cent.) and the *ethyl* compound, $CEtBr(CO{\cdot}NH_2)_2$, at 161·5° (Found : C = 28·6; H = 4·3; Br = 38·27. Theo., C = 28·7; H = 4·3; Br = 38·26 per cent.).

CLXVII.—*Researches on Chromammines. Part I. Salts of Nitro- and Other Dyes.*

By Herbert Joseph Seymour King.

It was shown previously (J., 1922, **121**, 1723) that substantive nitro-dyes (picric acid, aurantia, and naphthol yellow N and S) do not contain chelate groups capable of replacing ammonia in the

co-ordination complex of a cobaltammine salt. These dyes are thereby differentiated from mordant dyes of the quinoneoxime, alizarin, and azosalicylic acid series, which have been shown by Morgan and Main Smith to contain such groups.

To ascertain whether these relationships are independent of the nature of the metallic atom, the chromammine salts of the nitro-dyes, nitroso-β-naphthol, alizarin, and picramic acid have now been investigated. The results show that dyes containing chelate groups readily displace ammonia from the chromammine as from the cobaltammine complex, and confirm the conclusion that nitro-dyes do not contain such groups.

The chloropentammino- and hexammino-chromic salts of the four nitro-dyes are closely similar in appearance and properties to the corresponding cobaltammines. The table on page 1332 shows, for all the salts investigated, the percentage of ammonia lost at 100° (compare corresponding table for cobaltammines, *loc. cit.*). The chromammine salts of the nitro-dyes are almost as stable towards heat as the cobaltammines, and in this respect may be contrasted with those of nitroso-β-naphthol.

On boiling the chromammine salt of a nitro-dye with water, three ammonia molecules from a hexammine, or two from a pentammine, are evolved in about 20 minutes, with complete precipitation of chromium as chromic hydroxide. The remaining ammonia is evolved much more slowly, having combined with the acid radicals to form ammonium salts. The preferential formation of the ammonium rather than the chromic salt of the dye clearly differentiates these compounds from those containing chelate groups.

The absence of co-ordination between tervalent cobalt or chromium and nitro-groups has been further illustrated in the case of the chloropentamminocobaltic and hexamminochromic salts of 2 : 3 : 6-trinitrophenol. The former is the most stable towards heat of the salts investigated, losing no ammonia at 100°.

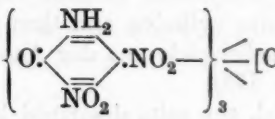
In view of the absence of chelation, the compound is probably $\{C_6H_2(NO_2)_3\cdot O—\}_2<[Co(NH_3)_5Cl]$ (I) rather than

$$\{O:C_6H_2(NO_2)_2:NO_2—\}_2<[Co(NH_3)_5Cl] \text{ (II.)}$$

The behaviour of potassium nitroso-β-naphthoxide towards chromammine solutions is almost identical with that towards the corresponding cobaltammines (Morgan and Main Smith, J., 1921, **119**, 708). The hexamminochromic salt is obtained analytically pure, but on heating at 100° or on boiling with water it readily parts with its ammonia, forming insoluble chromic nitroso-β-naphthoxide. The chloropentamminochromic salt is much less stable, losing four molecular proportions of ammonia at the ordinary temperature.

Attempts to prepare normal hexamminochromic alizarinate were unsuccessful, only the mono-salt being obtained. This is remarkable, since mono-alizarinates have hitherto been prepared only by precipitation from alcoholic solutions (A. G. Perkin, J., 1899, **75**, 434). Evidently the condition which inhibits the formation of insoluble monopotassium alizarinate in aqueous solution does not operate so far as the hexammino-base is concerned. 2-Hexamminochromic alizarinate is much less stable than the chromammines of nitro-dyes, but, as would be expected from the fact that the β-hydroxyl in alizarin is a normal salt-forming group, there is little tendency for the compound to lose all its ammonia with formation of 2-chromic alizarinate (Morgan and Main Smith, J., 1922, **121**, 160).

Hexamminochromic picramate is a chromammine salt of the same type as those of the nitro-dyes. Its stability towards heat and the preferential formation of ammonium rather than chromic picramate when it is boiled with water indicate the absence of a chelate grouping. As several instances of chelation in compounds containing an amino-group in the ortho-position to the co-ordination complex have been recorded by Morgan and Main Smith and by Morgan and Moss (J., 1922, **121**, 168, 2864), this result may be regarded as an indication that picramic acid has a para-quinonoid structure, with the amino-group in the meta-position to the co-ordination complex.

(III.)  $[Cr(NH_3)_6]$.

The aquopentamminocobaltic salt of naphthol yellow S was previously found to be unobtainable by the method of double decomposition (*loc. cit.*). On treating the acid with the alkaline solution obtained from aquopentamminocobaltic chloride and moist silver oxide, two instead of three molecules combined with two of hydroxide, hydroxopentamminocobaltic 2 : 4-dinitro-α-naphthoxide-7-sulphonate being formed. Thus the alkaline solution probably contains hydroxopentamminocobaltic hydroxide. Similarly, the alkaline solution obtained from chloropentamminochromic chloride and moist silver oxide gives with picric acid solution hydroxo- instead of aquo-pentamminochromic picrate. The hydroxopentamminochromic series, of which only the dithionate has been previously described (Jörgensen, *J. pr. Chem.*, 1882, [ii], **25**, 419; Dubsky, *ibid.*, 1914, [ii], **90**, 99) is being further investigated.

The following table shows the percentage of its ammonia lost by each of the salts escribed below after heating at 100° for 3 hours :

	NH_3 per cent. Before heating.	After heating.	Lost.
Chloropentamminochromic picrate	13·90	13·64	1·9
„ dipicrylamide	8·04	4·87	39·4
Chloropentamminochromic 2 : 4-dinitro-α-naphthoxide	12·03	10·14	15·7
Chloropentamminochromic 2 : 4-dinitro-α-naphthoxide-7-sulphonate	16·16	14·86	8·0
Hexamminochromic picrate	12·05	11·43	5·1
„ dipicrylamide	6·40	6·24	2·5
„ 2 : 4-dinitro-α-naphthoxide	10·04	9·60	4·4
„ 2 : 4-dinitro-α-naphthoxide-7-sulphonate	13·65	10·46	23·4
Chloropentamminocobaltic 2 : 3 : 6-trinitrophenoxide	13·49	13·49	0
Hexamminochromic 2 : 3 : 6-trinitrophenoxide	Decomposes		
„ 1 : 2-naphthaquinone-1-oximate (1-nitroso-β-naphthoxide)	13·36	0	100
2-Hexamminochromic 1 : 2-dihydroxyanthraquinone	10·83	2·95	72·8
Hexamminochromic picramate	13·69	9·21	32·7
Hydroxopentamminocobaltic 2 : 4-dinitro-α-naphthoxide-7-sulphonate	16·96	16·29	4·0
Hydroxopentamminochromic picrate	12·95	11·03	14·8
„ dipicrylamide	7·68	5·57	27·5

EXPERIMENTAL.

Hexamminochromic nitrate and chloropentamminochromic chloride were readily obtained in quantity by gradually adding, with stirring, powdered anhydrous chromic chloride to excess of liquid ammonia in a Dewar cylinder, and then proceeding as indicated by Biltz ("Übungsbeispiele aus der Anorganischen Experimental Chemie," 1913, p. 174).

Unless otherwise stated, the salts described below were precipitated at room temperature, collected forthwith, washed with ½ to 1 litre of water (all being sparingly soluble), and dried in a vacuum over soda-lime for 5 days. The chloropentamminochromic salts were obtained by double decomposition between saturated solutions of chloropentamminochromic chloride and the theoretical amount of the ammonium salt of the acid. The hexamminochromic salts were prepared by double decomposition between saturated solutions of hexamminochromic nitrate and 100 per cent. excess of the ammonium or sodium salt of the acid, unless otherwise stated.

I. *Chloropentamminochromic Salts of Nitro-dyes.*

Chloropentamminochromic picrate, large, anhydrous, orange needles, could be recrystallised from hot water, in which it was sparingly soluble (Found: Cr = 8·47; NH_3 = 13·90; N = 24·50; Cl = 5·58. $[Cr(NH_3)_5Cl]\{C_6H_2O_7N_3\}_2$ requires Cr = 8·27; NH_3 = 13·54; N = 24·51; Cl = 5·64 per cent.). The compound was very stable,

losing only 0·25 mol. of ammonia at 140°. On boiling with water, two of the five molecular proportions of ammonia were evolved in 20 minutes, with precipitation of chromic hydroxide. The remainder was evolved at the rate of 0·3 mol. in an hour. This compound is referred to by Jörgensen (*J. pr. Chem.*, 1879, [ii], 20, 125), but no analyses are recorded.

Chloropentamminochromic dipicrylamide was an anhydrous, amorphous, crimson compound, somewhat unstable on heating (see table) (Found: Cr = 5·34; NH_3 = 8·04; N = 25·71; Cl = 3·36. $[Cr(NH_3)_5Cl]\{C_{12}H_4O_{12}N_7\}_2$ requires Cr = 4·96; NH_3 = 8·12; N = 25·38; Cl = 3·38 per cent.).

Chloropentamminochromic 2 : 4-*dinitro-α-naphthoxide*, an amorphous, brick-red compound, was hexahydrated, but only 3 mols. of water were lost at 110° (Found: Cr = 7·41; NH_3 = 11·49; N = 16·79; Cl = 4·42. $[Cr(NH_3)_5Cl]\{C_{10}H_5O_5N_2\}_2,6H_2O$ requires Cr = 6·96; NH_3 = 11·40; N = 16·88; Cl = 4·75 per cent.).

Chloropentamminochromic 2 : 4-*dinitro-α-naphthoxide-7-sulphonate* separated in minute, bright yellow needles. Two only of the 4 mols. of water are lost at 100° (Found: Cr = 9·91; NH_3 = 16·21; N = 19·03; Cl = 6·68. $[Cr(NH_3)_5Cl]_2\{C_{10}H_4O_8N_2S\}_2,4H_2O$ requires Cr = 9·99; NH_3 = 16·35; N = 18·83; Cl = 6·81 per cent.).

II. *Hexamminochromic Salts of Nitro-dyes.*

Hexamminochromic picrate consists of masses of small, yellow needles. The air-dried product was hydrated ($2\frac{1}{2}H_2O$) and gave the anhydrous salt when dehydrated over phosphoric oxide in a vacuum (Found: Cr = 6·29; NH_3 = 12·05; N = 24·79. $[Cr(NH_3)_6]\{C_6H_2O_7N_3\}_3$ requires Cr = 6·20; NH_3 = 12·19; N = 25·06 per cent.). On boiling with water, three of the six mols. of ammonia were evolved in 20 minutes, with precipitation of the chromium as chromic hydroxide. The remaining ammonia was evolved at the rate of 1·5 mols. in an hour. The compound was completely decomposed on boiling for an hour with excess of ammonia, the chromium being deposited as chromic hydroxide.

This salt is mentioned by Ephraim and Mosimann (*Ber.*, 1922, 55, [*B*], 1615), who give a partial analysis.

Hexamminochromic dipicrylamide, a scarlet, amorphous salt, was hydrated ($2\frac{1}{2}H_2O$) when air-dried (Found: Cr = 3·12; NH_3 = 6·40; N = 24·54; H_2O = 3·10. $[Cr(NH_3)_6]\{C_{12}H_4O_{12}N_7\}_3,2\frac{1}{2}H_2O$ requires Cr = 3·44; NH_3 = 6·75; N = 24·99; H_2O = 2·98 per cent.).

Hexamminochromic 2 : 4-*dinitro-α-naphthoxide* was precipitated from 50 per cent. excess of the ammonium salt as an amorphous, brick-red, hydrated compound. When air-dried, it contained 8 mols. of water, of which 4 mols. were removed at 100° (Found:

Cr = 4·94; NH_3 = 10·04; N = 16·63; $C_{10}H_5O_5N_2$ = 70·41. $[Cr(NH_3)_6]\{C_{10}H_5O_5N_2\}_3,8H_2O$ requires Cr = 5·21; NH_3 = 10·24; N = 16·85; $C_{10}H_5O_5N_2$ = 70·10 per cent.). The acid radical was estimated by treating the compound with cold concentrated sulphuric acid, when it immediately decomposed, insoluble 2 : 4-dinitro-α-naphthol and hexamminochromic sulphate being formed.

Hexamminochromic 2 : 4 - *dinitro-α-naphthoxide* - 7 - *sulphonate*, obtained as bright yellow needles, when air-dried, contained 12 mols. of water, of which 10 mols. were lost at 100° (Found: Cr = 7·44; NH_3 = 13·65; N = 17·11. $[Cr(NH_3)_6]_2\{C_{10}H_4O_8N_2S\}_3,12H_2O$ requires Cr = 7·12; NH_3 = 13·98; N = 17·26 per cent.). After boiling with ammonia for 2 hours (the solution being kept ammoniacal), the yellow chromammine had almost completely decomposed, with formation of chromic hydroxide, only 7 per cent. of the ammonia remaining.

III. *Ammines of* 2 : 3 : 6-*Trinitrophenol* (Meldola and Hay, J., 1909, **95**, 1380).

Chloropentamminocobaltic 2 : 3 : 6-*trinitrophenoxide* (formula I or II) was obtained as an amorphous, bright scarlet precipitate on mixing equivalent solutions of potassium 2 : 3 : 6-trinitrophenoxide and chloropentamminocobaltic chloride, and cooling in ice (Found: Co = 9·07; NH_3 = 13·49; N = 24·14. $[Co(NH_3)_5Cl]\{C_6H_2O_7N_3\}_2$ requires Co = 9·28; NH_3 = 13·40; N = 24·24 per cent.).

Hexamminochromic 2 : 3 : 6-*Trinitrophenoxide*.—This amorphous, orange precipitate was produced immediately on filtering hexamminochromic hydroxide solution (obtained by triturating hexamminochromic bromide with excess of moist silver oxide) into the calculated amount of ammonium 2 : 3 : 6-trinitrophenoxide (Found: Cr = 6·19; NH_3 = 12·34; N = 25·19. $[Cr(NH_3)_6]\{C_6H_2O_7N_3\}_3$ requires Cr = 6·20; NH_3 = 12·19; N = 25·06 per cent.). At 100° the compound became red and finally dark brown, losing 20 per cent. of its weight, evidently owing to decomposition of the organic radical. On boiling with water, 3 mols. of ammonia were evolved in ½ hour, with precipitation of chromic hydroxide and formation of soluble ammonium 2 : 3 : 6-trinitrophenoxide. Ammonia was then evolved at the rate of ¾ mol. in an hour.

IV. *Hexamminochromic Salts of Nitroso-β-naphthol, Alizarin, and Picramic Acid.*

Hexamminochromic 1-*nitroso-β-naphthoxide* (1 : 2-*naphthaquinone*-1-*oximate*) was obtained, on mixing saturated solutions of hexamminochromic nitrate and 100 per cent. excess of potassium

nitroso-β-naphthoxide, as a green, amorphous precipitate (Found: Cr = 7·24; NH_3 = 13·36; N = 16·87; H_2O = 9·45. $[Cr(NH_3)_6]\{C_{10}H_6O_2N\}_3,4H_2O$ requires Cr = 7·00; NH_3 = 13·76; N = 16·98; H_2O = 9·70 per cent.). On boiling with water, the whole of the ammonia was evolved in 45 minutes, leaving an insoluble, chocolate-brown precipitate of chromic nitroso-β-naphthoxide, which was also obtained on boiling the hexamminochromic salt with sodium hydroxide solution. In neither case was any chromic hydroxide precipitated.

At 100°, the salt lost 93 per cent. of its ammonia in 10 minutes, and the whole in 3 hours, again forming chromic nitroso-β-naphthoxide.

When potassium nitroso-β-naphthoxide solution was treated with a solution of the calculated amount of chloropentammino-chromic chloride, a scanty, greenish-brown precipitate was obtained. The ratio of chromium to ammonia showed that 80 per cent. of the ammonia of the chloropentammino-salt had been lost. After heating at 100° for 3 hours, however, 1 per cent. of ammonia (¼ mol.) remained.

2-Hexamminochromic 1 : 2 - *Dihydroxyanthraquinone* (*Acid Hexamminochromic Alizarinate*).—By interaction of hexamminochromic nitrate and dipotassium alizarinate, even with the former in excess, a product intermediate between the acid and normal salts was obtained. The violet acid salt was prepared by triturating recrystallised alizarin for an hour, in absence of daylight, with the calculated amount of hexamminochromic hydroxide solution. It was washed successively with water, cold pyridine (in which alizarin is very soluble), and alcohol, dried in air and finally in a vacuum over soda-lime. This product, which imparted a reddish-violet tint to water, and closely resembled in colour monopotassium alizarinate, was decomposed by concentrated hydrochloric acid, forming free alizarin (Found: Cr = 5·61; NH_3 = 10·83; $C_{14}H_7O_4$ = 76·85; H_2O = 6·44. $[Cr(NH_3)_6]\{C_{14}H_7O_4\}_3,3\frac{1}{2}H_2O$ requires Cr = 5·56; NH_3 = 10·93; $C_{14}H_7O_4$ = 76·76; H_2O = 6·75 per cent.). Considerable excess of alkali was required to remove the ammonia completely. On boiling with water, 3 mols. of ammonia were removed in 25 minutes, 5 in 80 minutes, and the whole only on very prolonged boiling. After extracting the residue with alcoholic pyridine, pure 2-chromic alizarinate was not obtained, owing to partial decomposition into insoluble normal chromic alizarinate.

Hexamminochromic Picramate (Formula III).—Hexamminochromic hydroxide, from 2 grams of bromide, was filtered into the calculated amount (3 grams) of picramic acid converted to the ammonium salt, in aqueous solution. The chocolate-brown,

amorphous precipitate was anhydrous after drying in a vacuum over phosphoric oxide. It was sparingly soluble in cold, fairly readily soluble in hot water, the solution being red. Its solutions in strong sulphuric acid and in cold aqueous sodium hydroxide were brown and red, respectively. It was decomposed by concentrated hydrochloric acid, forming picramic acid (Found: Cr = 7·10; NH_3 = 13·69; N = 28·24. $[Cr(NH_3)_6]\{C_6H_4O_5N_3\}_3$ requires Cr = 6·95; NH_3 = 13·65; N = 28·07 per cent.).

On boiling 0·2 gram with 250 c.c. of water, 3·1 mols. of ammonia were evolved in 30 minutes, with precipitation of chromic hydroxide. Evolution of ammonia then proceeded at the rate of 0·75 mol. in an hour. Boiling with aqueous ammonia yielded a red solution of ammonium picramate and a precipitate of chromic hydroxide.

V. *Hydroxopentamminocobaltic and Hydroxopentamminochromic Salts of Nitro-dyes.*

Hydroxopentamminocobaltic 2 : 4-*Dinitro-α-naphthoxide-7-sulphonate.*—Aquopentamminocobaltic chloride (2·5 grams, 2 mols.) was converted into hydroxide by triturating with excess of moist silver oxide and the solution was filtered into 3·4 grams (2 mols.) of the sulphonic acid in 300 c.c. of water. An amorphous, finely divided, orange precipitate (3·9 grams) formed immediately, leaving the mother-liquor almost colourless. The compound was trihydrated, but only one-sixth of the water was removed at 100° (Found: Co = 11·75; NH_3 = 16·96; N = 19·79; S = 6·33. $[Co(NH_3)_5OH]_2\{C_{10}H_4O_8N_2S\}_2,3H_2O$ requires Co = 11·79; NH_3 = 17·02; N = 19·60; S = 6·41 per cent.). Only 2 mols. of sulphonic acid combined with 2 mols. of hydroxide, even when 4 mols. of the former were present.

Hydroxopentamminochromic Picrate.—Aquopentamminochromic picrate was not obtained by the action of "aquopentamminochromic hydroxide" on picric acid solution, even when 200 per cent. excess of picric acid was employed. The pure hydroxo-salt was obtained by filtering the hydroxide from 4 grams of chloropentamminochromic chloride into the calculated amount (7·52 grams) of picric acid in 900 c.c. of water; 7·8 grams of yellow acicular crystals were obtained (Found: Cr = 7·98; NH_3 = 12·95; N = 23·90; H_2O = 6·89. $[Cr(NH_3)_5OH]\{C_6H_2O_7N_3\}_2,2\frac{1}{2}H_2O$ requires Cr = 7·93; NH_3 = 12·98; N = 23·51; H_2O = 6·87 per cent.). The compound was completely dehydrated when kept in a vacuum over phosphoric oxide for a week, losing also 2 per cent. of its ammonia.

Hydroxopentamminochromic dipicrylamide, a bright scarlet, amorphous, hydrated precipitate, was produced by mixing solutions of aquopentamminochromic hydroxide and ammonium dipicrylamide

(3 mols.) (Found: Cr = 4·86; NH_3 = 7·68; N = 25·23; H_2O = 1·41. $[Cr(NH_3)_5OH]C_{12}H_4O_{12}N_7{}^1/_2,H_2O$ requires Cr = 4·96; NH_3 = 8·12; N = 25·38; H_2O = 1·72 per cent.).

When dipicrylamine (3 mols.) was triturated with aquopentamminochromic hydroxide solution for 2 hours, no reaction occurred.

On boiling with sodium hydroxide solution, the chromammines of picric acid and of dipicrylamine, like the cobaltammines, continued to evolve ammonia at a decreasing rate long after all the chrommammine ammonia had been liberated. Thus in the case of chloropentamminochromic picrate, after 3½ hours, one-half of the nitrogen of the picrate radicals had been evolved as ammonia. As with the corresponding cobaltammines, a normal end-point was obtained on boiling with water and calcium carbonate.

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UNIVERSITY OF LONDON. [*Received, March 20th*, 1924.]

CLXVIII.—*Synthesis of Amygdalin.*

By RAY CAMPBELL and WALTER NORMAN HAWORTH.

THE structure of the sugar residue in amygdalin was determined by Haworth and Leitch (J., 1922, **121**, 1921) and the identity of amygdalin biose with gentiobiose was established by Haworth and Wylam (J., 1923, **123**, 3120). In the latter paper, a preliminary announcement was made of the synthesis of ethyl heptaacetylamygdalinate, of which a more complete account is now communicated along with the further successive stages leading to the complete synthesis of amygdalin. Other workers have meanwhile confirmed our previous results. From polarimetric data, Hudson (*J. Amer. Chem. Soc.*, 1924, **46**, 483) calculated the molecular rotation of amygdalin biose, which is in agreement with that of β-gentiobiose, and therefore he drew by an independent method the same conclusion as ourselves. Hudson suggested a possible method of synthesising amygdalin, the first experimental stage of which had, however, when his paper appeared, already been communicated by Haworth and Wylam (*loc. cit.*).

Gentiobiose having been synthesised by Bourquelot, Hérissey, and Coirre (*Compt. rend.*, 1913, **157**, 732), its simultaneous bromination and acetylation were accomplished by dissolving the sugar in acetic anhydride saturated with hydrogen bromide. The solid

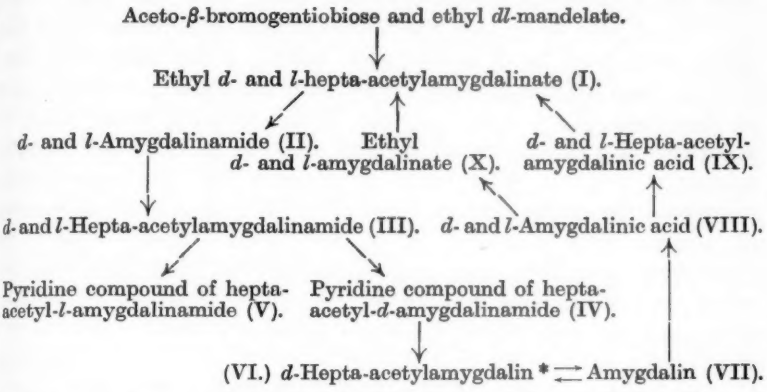
hepta-acetyl-β-bromogentiobiose was condensed with ethyl *dl*-mandelate in presence of silver oxide, and the product, colourless needles, m. p. 205°, was characterised as hepta-acetyl *dl*-amygdalinic ester (I) identical in all respects with two specimens of this substance prepared by the following alternative methods (*a* and *b*) from amygdalin: (*a*) Amygdalinic acid (VIII) was first obtained from amygdalin by Liebig and Wöhler (*Annalen*, 1837, **22**, 1), a transformation which has been shown by Dakin to be accompanied by racemisation of the mandelic acid residue (J., 1904, **85**, 1512). Amygdalinic acid was acetylated by Schiff (*Annalen*, 1870, **154**, 350) and we have found that hepta-acetylamygdalinic acid (IX) undergoes direct esterification by solution in ethyl alcohol. (*b*) A solution of barium amygdalinate was mixed with silver sulphate and the resulting silver amygdalinate digested with ethyl iodide, followed by acetylation of the ethyl amygdalinate (X).

Amygdalinamide (II), derived from the above acetylated ester (I) by treatment with an alcoholic solution of ammonia, was isolated as a colourless, brittle solid. On re-acetylation in presence of pyridine, hepta-acetylamygdalinamide was isolated as needles in two isomeric forms having $[\alpha]_D$ — 68·6° and — 49·7° and melting respectively at 166—167° and 152—153°, both of which specimens contained one molecule of combined pyridine. These stereoisomerides were separated by careful fractional crystallisation from alcohol, a procedure which involved a direct resolution. The crystals melting at 166—167° were shown to be hepta-acetyl-*d*-amygdalinamide (IV) and it is probable that the compound melting at the lower temperature will prove to be the *l*-isomeride (V), from which we hope to obtain *neo*amygdalin.

The search for conditions leading to the elimination of water from the amide proved difficult, but eventually this step was achieved by digesting the acetylated amide (m. p. 166—167°) in xylene solution with phosphoric oxide. On crystallisation, the product gave rise to some unchanged acetylated amide, but was largely converted into hepta-acetylamygdalin (VI). No trace of the corresponding derivative of *neo*- or *iso*-amygdalin was observed.

The remaining stage in the complete synthesis of amygdalin was the conversion of hepta-acetylamygdalin, which was originally prepared from natural amygdalin by Caldwell and Courtauld (J., 1907, **91**, 671), into amygdalin. This last result has already been attained by E. Fischer and M. Bergmann (*Ber.*, 1917, **50**, [*B*], 1065) by de-acetylation of acetylamygdalin with methyl-alcoholic ammonia. The following scheme summarises the successive stages of the synthesis and shows also the relationships which

have been established with the compounds prepared from natural amygdalin. It will be seen that several of the steps resemble those of Fischer and Bergmann's synthesis of prulaurasin (*loc. cit.*).


Aceto-β-bromogentiobiose and ethyl dl-mandelate.
Ethyl d- and l-hepta-acetylamygdalinate (I).
d- and l-Amygdalinamide (II).
Ethyl d- and l-amygdalinate (X).
d- and l-Hepta-acetyl-amygdalinic acid (IX).
d- and l-Hepta-acetylamygdalinamide (III).
d- and l-Amygdalinic acid (VIII).
Pyridine compound of hepta-acetyl-l-amygdalinamide (V).
Pyridine compound of hepta-acetyl-d-amygdalinamide (IV).
(VI.) d-Hepta-acetylamygdalin *
Amygdalin (VII).

Zemplén (*Ber.*, 1924, **57**, [*B*], 698) has confirmed the results of Haworth and Wylam's work on the identity of the amygdalin biose with gentiobiose. He communicates also a synthesis of hepta-acetylamygdalinic ester differing in experimental method from that of Haworth and Wylam (*loc. cit.*), but no analysis of the carbon and hydrogen content of his product is given, and the specific rotation quoted ($[\alpha]_D$ — 9·73°) differs widely from our value ($[\alpha]_D$ — 62·0°), which is in agreement with that for the same product derived from natural sources. We have refrained from establishing a comparison between specimens of amygdalinic acid or its acetyl derivative derived from synthetic and natural sources, because the physical constants of these substances, even when prepared from amygdalin, are indefinite.

Experimental.

Acetylation of dl-*Amygdalinic Acid* (*VIII*) *and Isolation of Ethyl* dl-*Hepta-acetylamygdalinate* (*I*).—A mixture of 10 grams of amygdalinic acid, 50 c.c. of pyridine, and 100 c.c. of acetic anhydride was kept for several minutes until the initial heating effect had abated and was then boiled under reflux for 3 hours. The brown oil that separated on pouring the cooled mixture into iced water was agitated therein for some time, the supernatant, aqueous liquid decanted, and the oil caused to solidify by stirring. The brown

* Although what is here described as *d*-hepta-acetylamygdalin contains the lævorotatory mandelic acid residue, as does also amygdalin, it is assigned to the *d*-series for the same reasons as those given by Clough (J., 1918, **113**, 526) and by Freudenberg, Brauns, and Siegel (*Ber.*, 1923, **56**, [*B*], 193).

solid was powdered, washed with water, and dried. It did not crystallise well from any solvent, but a colourless, amorphous solid was obtained from a mixture of equal parts of ethyl alcohol and water (Found: $CH_3{\cdot}CO = 20$. Calc., 39·1 per cent.). On account of this deficiency the whole of the amorphous solid was again acetylated for 3 hours, with boiling acetic anhydride containing fused sodium acetate. The crude solid product was isolated as described above and dissolved in hot alcohol, from which it separated as a colourless, amorphous mass, m. p. 175—180°, readily soluble in acetone, chloroform, or benzene, and sparingly soluble in ether. On crystallisation from ethyl alcohol, colourless rosettes of needles were collected, m. p. 205°, $[\alpha]_D$ — 62·4°, — 62·1° in chloroform ($c = 0{\cdot}8$), and the compound was insoluble in water, ether, or cold alcohol, soluble in hot alcohol, acetone, or chloroform, and did not reduce Fehling's solution (Found: C = 54·25; H = 5·9; OEt = 5·6; $CH_3{\cdot}CO{\cdot} = 38{\cdot}9$. $C_{36}H_{46}O_{20}$ requires C = 54·1; H = 5·76; OEt = 5·65; $CH_3{\cdot}CO{\cdot} = 37{\cdot}7$ per cent.). These analyses indicate, not hepta-acetylamygdalinic acid, but its ethyl ester. The simple operation of solution in alcohol had thus effected esterification.

Preparation of Ethyl dl-*Amygdalinate* (*X*) *and its Acetylation.*—Pure dry barium amygdalinate (1 mol.) (Dakin, J., 1904, **85**, 1512) was dissolved in the minimum volume of hot water and mixed with a saturated aqueous solution of silver sulphate (1 mol.); the filtrate from barium sulphate was concentrated under diminished pressure in a dark room, decolorised with charcoal, and evaporated. The solid silver salt was thoroughly dried with alcohol, powdered, and digested for 3 hours with a large excess of ethyl iodide and absolute alcohol (equal vols.), the latter being added to prevent incrustation of the silver salt and silver iodide. After filtration and evaporation, a syrup remained which, on removal of the last traces of solvent, changed into a white, amorphous solid. Although soluble in water and ethyl and methyl alcohol, the compound did not crystallise from these solvents; $[\alpha]_D = -78{\cdot}0°$ (Found: C = 52·11; H = 6·29; OEt = 9·8. $C_{22}H_{32}O_{13}$ requires C = 52·38; H = 6·35; OEt = 9·0 per cent.).

Acetylation. The above specimen of ethyl amygdalinate was boiled under reflux during 4 hours with a mixture of acetic anhydride and fused sodium acetate and, on pouring into water, the oily product gradually solidified; it crystallised from hot ethyl alcohol in rosettes of small needles, m. p. 202°, and, after recrystallisation, 205°. Its identity with ethyl hepta-acetylamygdalinate was confirmed by its specific rotation and by the melting point of the mixture with the specimen prepared as described above.

On one occasion, a by-product was an isomeride which, recrystallised twice, had m. p. 184—186° and $[\alpha]_D$ — 28·6°.

Synthesis of Ethyl dl-*Hepta-acetylamygdalinate* (*I*).—This ester was synthesised by shaking a paste of dried ethyl *dl*-mandelate (20 grams), hepta-acetyl-β-bromogentiobiose (4·7 grams), and silver oxide (10 grams) for 20 hours at atmospheric temperature. The dry chloroform extract of the product, which gave no test for the presence of a brominated sugar, was decolorised with charcoal and evaporated under diminished pressure, when a mobile syrup remained. The excess of ethyl mandelate was distilled at 94°/0·02 mm. and the residue, a viscid syrup, was dissolved in hot absolute alcohol; on cooling and nucleating with a specimen of ethyl hepta-acetylamygdalinate prepared from natural amygdalin, rosettes of colourless needles, sintering at 195° and melting at 200°, were obtained. The mother-liquors were evaporated and the residual syrup gave, on digestion with dry ether, a faintly coloured solid which was dried and recrystallised from absolute alcohol, when a further crop of needles, m. p. 198°, was obtained. The syrupy product recovered from the ethereal extract was acetylated by heating with acetic anhydride for 2 hours; the solid isolated on pouring the cooled mixture into cold water crystallised from alcohol in needles, 202—204°. The three crops of needles were identical in properties and therefore they were united and recrystallised. The compound then melted at 205°, alone or mixed with ethyl hepta-acetylamygdalinate (m. p. 205°) * from natural sources (Found: C = 53·8; H = 5·93. Calc. for $C_{36}H_{46}O_{20}$, C = 54·1; H = 5·76 per cent.). The specific rotation in dry chloroform was $[\alpha]_D$ — 62·0°, whilst the specimen prepared direct from amygdalin showed $[\alpha]_D$ — 62·1°. Having established beyond doubt the identity of the synthetic ester with that derived from amygdalin, we were able to augment our supply of material from the latter source for subsequent work.

Synthesis of dl-*Amygdalinamide* (*II*) *and Resolution of its Hepta-acetyl Derivative* (*III*).—A suspension of hepta-acetylamygdalinic ester in dry methyl alcohol was saturated with ammonia at 0° and shaken for 40 hours; on two other occasions during this period, the stoppered vessel was opened and more dry ammonia admitted. The pale yellow liquid was filtered, and evaporated under diminished pressure, leaving a straw-coloured, viscid syrup, three successive digestions of which with hot ethyl acetate, followed by decantation after cooling, extracted completely the acetamide formed as a by-product of the de-acetylation. The last traces of ethyl acetate were removed by heating in a vacuum, and the syrup

* The melting points given in this paper are "uncorrected."

frothed and gave a colourless, brittle solid, $[\alpha]_D$ — 77·0°, which was soluble in water or pyridine, slightly soluble in hot alcohol, and insoluble in chloroform or ether (Found: N = 3·17. Calc. for amygdalinamide, N = 2·95 per cent.).

Acetylation and Resolution.—The amide (15 grams), dissolved in pyridine (90 c.c.), was heated for 4 hours with acetic anhydride (180 c.c.), the cooled solution poured into 750 c.c. of water, and the precipitated oil washed with a similar volume of water. The product, which soon crystallised, separated from hot alcohol in slender needles, m. p. 140—145°. Fractional crystallisation led to a separation of two isomerides, m. p. 166—167° and 152—153°, and $[\alpha]_D$ — 68·6° and — 49·7° (in chloroform), respectively (Found: for first isomeride, C = 55·5; H = 5·65; for second isomeride, C = 55·23; H = 5·42. Calc. for hepta-acetylamygdalinamide + 1 mol. pyridine, C = 55·19; H = 5·66 per cent.).

Conversion of Synthetic d-*Hepta-acetylamygdalinamide* (*IV*) *into* d-*Hepta-acetylamygdalin* (*VI*).—The specimen of hepta-acetylamygdalinamide melting at 166—167° (1 gram) was dissolved in dry xylene, 2 grams of phosphoric oxide were added, and the mixture was boiled under reflux for 3 hours, filtered, and the solution evaporated in a vacuum. The residual syrup was slightly coloured and after solution in ethyl alcohol and decolorisation with charcoal, fine, colourless needles were deposited, m. p. 156—160°. The dark residue of phosphoric oxide was extracted with chloroform and this gave a second crop of crystals, m. p. 154—159°. These two crops were united and recrystallised three times from ethyl alcohol, when needles were isolated melting at 169° with slight sintering at 168° (Found: C = 54·4; H = 5·43. Calc. for $C_{34}H_{41}O_{18}N$, C = 54·33; H = 5·46 per cent.).

The analytical data and properties were in complete agreement with those of hepta-acetylamygdalin prepared from natural sources (Caldwell and Courtauld, *loc. cit.*) and, moreover, the optical activity was $[\alpha]_D$ — 36·2° (in ethyl acetate), whilst the rotation of hepta-acetylamygdalin prepared from amygdalin was — 35·8°. A mixed melting-point determination of the synthetic product with acetylated amygdalin (m. p. 169°) showed no depression.

The conversion of acetyl amygdalin into amygdalin by deacetylation has already been effected by Fischer and Bergmann (*loc. cit.*), and, using the above specimen (VI), we have isolated amygdalin by the same procedure (m. p. 208—212°).

The authors express their thanks to the Department of Scientific and Industrial Research for a grant for the purchase of special

apparatus, to the Council of Armstrong College for a Fellowship enabling one of us to participate in this work, and to Mr. B. Wylam, M.Sc., for assistance in preparing gentiobiose.

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CLXIX.—*Derivatives of a New Form of Mannose.*

By JAMES COLQUHOUN IRVINE and WILLIAM BURT.

THE expression "γ-sugar" has meanwhile a general significance and is applied to varieties of aldoses and ketoses in which the oxygen ring is displaced from the stable position. Sugars which are similar in their properties, in their mode of formation, and in their variation from a normal type, are thus classified together in a manner which is as satisfactory as present knowledge permits. Although obvious disadvantages are attached to the use of this nomenclature, no alternative is possible until the position of the internal ring in each reducing sugar has been experimentally determined. The attainment of this condition necessary for a complete classification of sugars is still remote.

We are engaged with the further study of various γ-sugars and now submit the results obtained in the case of mannose. So far, this sugar has been converted into only one methylmannoside, termed the α-form, and the corresponding β-form is unknown. Conditions are now prescribed whereby a mixture of two new methylmannosides can be obtained which displays properties similar to those of Fischer's γ-methylglucoside, thus bringing mannose into line with glucose, fructose, and galactose. The name "γ-methylmannoside" as now used refers to a preparation containing two stereoisomeric forms of the compound which differ from each other in the position of the methyl group, and from α-methylmannoside in the linking of the internal ring.

This displacement of the oxygen-ring from the normal stable position is not revealed by hydrolysis, as the liberated sugar at once reverts to the ordinary variety of mannose. We have accordingly converted γ-methylmannoside successively into trimethyl- and tetramethyl γ-methylmannoside. These products retained the vigorous action on permanganate which is characteristic of the γ-type and consisted in each case of two stereoisomeric forms, but the isomerism was obliterated on hydrolysis. This gave tetramethyl γ-mannose, which resembles tetramethyl γ-glucose closely

and is distinct from the isomeride described by Irvine and Moodie (J., 1905, **87**, 1462).

Tetramethyl mannose from

α-Methylmannoside.	γ-Methylmannoside.
Syrup, b. p. 187°/19 mm.	Crystalline, b. p. 190°/10 mm.
$[\alpha]_D$ in MeOH + 17·2°	+ 48·5°
No action on permanganate.	Vigorous reduction.
Reacts slowly with acid methyl alcohol at 100°.	Reacts rapidly at 15°.

The sharp distinction between the new derivatives and those conforming to the stable type will be evident from the quantitative data given in the experimental part, but the following special features may be mentioned. γ-Methylmannoside has only a transient existence and the manipulation of the compound is hampered, not only by its extreme instability to hydrolysts, but also by its spontaneous conversion into the α-form. Of two specimens of γ-methylglucoside which had been preserved for 5 years in sealed flasks, one was found to have undergone hydrolysis to give crystalline glucose but the other was still intact. In contrast with this behaviour, γ-methylmannoside is notably sensitive and apparently the oxygen linking alters its position whilst the reducing group remains substituted. This property, which is unique in the γ-glucosides so far studied, demanded that the methylations had to be completed within a few days. A further complication was the pronounced steric hindrance encountered in introducing the fourth alkyl group into γ-methylmannoside and it may be noted that this particular methoxyl group resisted the action of hydriodic acid except under much more drastic conditions than are usually employed.

Although derivatives of γ-mannose display abnormal rotations, it can no longer be assumed that, as in the case of glucose and fructose, a change of sign accompanies the alteration of structure to the γ-type. Curiously enough, the specific rotation of some preparations of γ-methylmannoside was identical with that of α-methylmannoside, but this is fortuitous and depends on the proportion of the two forms present in the mixture. The most striking optical difference is shown by the fully methylated compounds, the dextrorotation of the γ-type being practically the same in alcohol as in water. On the other hand, the specific rotation of the corresponding α-variety is nearly doubled when alcohol replaces water as the solvent. In this respect, the activity of γ-mannose derivatives is comparable with that of normal glucose derivatives, an observation which is important in view of Hudson's generalisations on activity in the sugar group. In view of the difficulties here indicated, we have been unable meanwhile to extend the

research in the direction of determining the precise position occupied by the oxydic ring in γ-mannose.

Experimental.

To facilitate description, it may be stated that pure dry organic solvents were used throughout, that the mannose was sifted through fine muslin, and that all evaporations were conducted under diminished pressure, the temperature being kept below 35°.

Condensation of Mannose with Methyl Alcohol.—Method I. The sugar was dissolved in the minimum quantity of hot water and mixed with a large excess of methyl alcohol previously saturated at 0° with hydrogen chloride. Condensation was effected at 15°, standard methods being employed to control the reaction and to isolate the products. Average result: a 60 per cent. yield of α-methylmannoside, the remainder consisting of a mannosidic syrup which was freed from the solid by extraction with small quantities of hot absolute alcohol. The extraction and evaporation of the solvent were repeated several times and ultimately the syrup was dissolved by shaking with cold ethyl acetate. After isolation, the compound was freed from traces of reducing sugar by treatment at 15° with methyl alcohol containing 0·5 per cent. of hydrogen chloride. The mannoside was again recovered and purified from ethyl acetate as in the case of γ-methylglucoside, when it was obtained as an extremely viscous syrup (Found: C = 43·12; H = 7·01; OMe = 15·6. $C_7H_{14}O_6$ requires C = 43·27; H = 7·22; OMe = 15·9 per cent.). In the particular preparation described, the rotation was much lower than when the compound was made by other methods. $[\alpha]_D^{20°}$ + 21·8° in ethyl alcohol (c = 4·344) and + 27·8° in water (c = 4·457).

The compound behaved as a glucoside, reduced neutral permanganate at once, and decomposed without distillation at 210°/0·01 mm. Hydrolysis to mannose was complete on heating at 100° with N/10-hydrochloric acid for 9 hours, but the mannoside was stable towards this reagent at 20°. Using N/50-acid at 100°, the rotation of the solution increased and then diminished, showing that two hydrolysable forms were present.

Method II. Details of a typical preparation of γ-methylmannoside are: 35 grams of mannose were dissolved in 700 grams of methyl alcohol containing 1 per cent. of hydrogen chloride by shaking at 15° for 3 hours. Fifteen hours thereafter the condensation was arrested and the product isolated precisely as in Fischer's preparation of γ-methylglucoside. Approximately one-half of the sugar was recovered unchanged, the remainder being converted into the new form of methylmannoside (Found: C = 43·30; H = 7·32;

OMe = 13·9 per cent.). The rotation of γ-methylmannoside which we consider to be the most trustworthy is $[\alpha]_D^{20°} = +80·2°$ for $c = 2·306$ in ethyl alcohol. This value is nearly identical with that shown by the α-form, but the isomerides are readily distinguished by their different stability towards acids as shown below :—

Solvent: $N/10$-Hydrochloric acid. $T = 100°$.

Time (mins.).	α-Methyl-mannoside.	Mixture of γ-methyl-mannosides.	Time (mins.).	α-Methyl-mannoside.	Mixture of γ-methyl-mannosides.
0	$[\alpha]_D$ + 79·4°	+ 79·4°	60	$[\alpha]_D$ + 77·6°	+ 22·3°
15	79·0	65·2	90	76·3	15·1
30	78·6	48·7	120	75·6	(constant)

The complete polarimetric record, when plotted on a curve, shows that the syrup consisted of two forms which were hydrolysed at different speeds. This explains the discrepancies in the rotations displayed by different preparations of the compound.

γ-Methylmannoside on keeping is gradually transformed into the crystalline α-variety, the change being detectable before the appearance of crystals by the rapid diminution of solubility in cold ethyl acetate.

Methylation of γ-Methylmannoside.—Unsatisfactory yields were obtained by the use of the methyl sulphate method and the product soluble in chloroform decomposed partly on distillation. *Trimethyl γ-methylmannoside* was, however, obtained by two applications of the silver oxide reaction and, after distillation under 0·3 mm., was isolated as a colourless syrup possessing the usual properties of a γ-glucoside (Found: C = 50·60; H = 8·76; OMe = 53·3. $C_{10}H_{20}O_6$ requires C = 50·85; H = 8·48; OMe = 52·5 per cent.).

Tetramethyl γ-Methylmannoside.—Five successive methylations were required to introduce the fifth alkyl group. The reactions were conducted in methyl iodide solution and the product was distilled after each treatment. This involved much experimental loss, as invariably a considerable undistillable residue remained in the flask. The product was a colourless, mobile liquid resembling tetramethyl γ-methylglucoside in properties. B. p. 141°/13 mm.; n_D 1·4482; $[\alpha]_D^{20°}$ + 24·9° in ethyl alcohol ($c = 4·046$), + 30·9° in acetone ($c = 4·134$), and + 22·6° in water ($c = 4·011$) (Found: C = 52·6; H = 8·7; OMe = 60·0. $C_{11}H_{22}O_6$ requires C = 52·8; H = 8·8; OMe = 62·0 per cent.).

The parallel experiments quoted below reveal that the specimen consisted of two forms of unequal stability and emphasise that tetramethyl γ-methylmannoside is much more easily hydrolysed than the corresponding α-isomeride.

Solvent: $N/10$-Hydrochloric acid. $T = 100°$; $c = 3$.

Time (mins.)		0	15	60	90	120
Tetramethyl α-methylmannoside	$[\alpha]_D$	+ 40·5°	40·3°	40·0°	39·8°	39·4°
Tetramethyl γ-methylmannoside	$[\alpha]_D$	+ 22·6°	22·8°	24·6°	11·3°	7·9° (constant)

Tetramethyl γ-Mannose.—Hydrolysis of the methylated γ-mannoside was effected under the conditions indicated above and the sugar was isolated as usual. On distillation, a little unchanged mannoside was collected, after which tetramethyl γ-mannose distilled at 190°/10 mm. as a viscous syrup which slowly crystallised in clusters of prisms.

No suitable recrystallising agent could be found (Found: C = 50·75; H = 8·29; OMe = 52·4. $C_{10}H_{20}O_6$ requires C = 50·85; H = 8·47; OMe = 52·5 per cent.). The superfused solid gave n_D 1·4647. $[\alpha]_D^{20°}$ + 47·4° in ethyl alcohol (c = 1·012) and + 48·5° in methyl alcohol (c = 1·010).

The sugar is characterised by the energy with which it attacks Fehling's solution and also permanganate. An indication of the unusual speed with which it forms two methylmannosides is given by the following figures:—

Solvent: Methyl alcohol containing 0·25 per cent. of hydrogen chloride. $T = 15°$.

Time (mins.) from solution	1	4	12	20	45	100
$[\alpha]_D^{15°}$	+37·8°	−1·9°	−13·8°	+13·6°	+23·7°	+33·6°

After 20 minutes the reducing action was negligible, but the rotation continued to increase to the constant value + 43·5°.

Conversion from γ- to α-Isomerides during Methylation.—A specimen of γ-methylmannoside, free from the α-form, was methylated by the methyl sulphate process. Although the tetramethyl methylmannoside obtained was analytically pure (Found: C = 52·76; H = 8·97; OMe = 61·2 per cent.), it was only in part hydrolysed by $N/10$-hydrochloric acid at 15°. On distillation of the resulting syrup, half of the material boiled at 139·5°/10 mm. and was identified as tetramethyl α-methylmannoside (m. p. 37°, n_D 1·4520). The remainder consisted of tetramethyl γ-mannose (Found: C = 50·98; H = 8·58; OMe = 52·2 per cent.). The same change proceeds, but to a much smaller extent, when the complete methylation is carried out by the silver oxide process.

Evidence indicating Autocondensation of γ-Mannose Derivatives.—In preparing γ-methylmannoside by the method involving concentrated hydrochloric acid a glucosidic syrup was occasionally (but not invariably) obtained which gave analytical figures agreeing approximately with those required for a dimannose. No methyl

group was present, but the compound was easily hydrolysed to give mannose in quantitative amount.

Further, when tetramethyl γ-mannose or its derivatives were distilled, a non-volatile residue invariably remained, even although the material had already passed through a distillation. These residues when purified formed a colourless glass which behaved sharply as a glucoside and showed a surprising uniformity in composition (Found : C = 52·86; H = 7·28; OMe = 32·53. $C_{16}H_{26}O_9$ requires C = 53·03; H = 7·18; OMe = 34·25 per cent.).

The view that the compound is a tetramethyl dimannose was confirmed by the observation that hydrolysis to give the corresponding sugar did not result in the loss of a methyl group. It is important to note that in the case of all methylated derivatives of γ-mannose which contain three or more methyl groups it is necessary, in estimating the alkyloxy-content, to heat with hydriodic acid to 145° at least. Under the usual conditions (135°) one methoxyl group remains unaffected.

Acknowledgment is due to the Carnegie Trust for a Research Scholarship held by one of us.

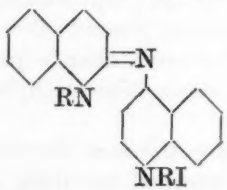
UNITED COLLEGE,
UNIVERSITY OF ST. ANDREWS. [*Received, April 11th*, 1924.]

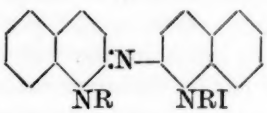
CLXX.—*The Synthesis of an Azocyanine.*

By FRANCES MARY HAMER.

IT should be possible to prepare analogues of the cyanine dyes in which the linking between the quinoline nuclei is effected, not by a methenyl group, but by a nitrogen atom : to such analogues, the name of *azocyanines* may be given. Thus corresponding with *iso*cyanine and pseudo*iso*cyanine, for example, we should have 1 : 1′-dialkyl-2 : 4′-azocyanine iodide (I) and 1 : 1′-dialkyl-2 : 2′-azocyanine iodide (II), respectively.

(I.)

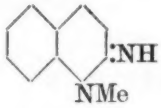




(II.)

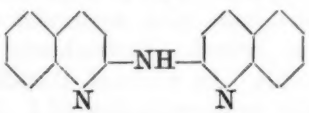
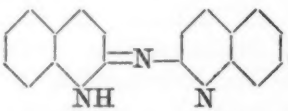
The 2 : 4′-azocyanine could not be prepared simply by replacing quinaldine methiodide in the *iso*cyanine condensation by 2-aminoquinoline methiodide. The inactivity of the latter substance is

also shown by its not condensing with 2-chloroquinoline or with formaldehyde; 2-aminoquinoline does unite with 2-chloroquinoline and therefore is more reactive than its methiodide. The pseudo-base (III) (Tschitschibabin, *Ber.*, 1921, **54**, [*B*], 822) thus contrasts with the analogous compound IV, to the existence of which Mills and Smith have attributed the greater reactivity of quinaldine methiodide as compared with quinaldine (J., 1922, **121**, 2724).

(III.)  (IV.)

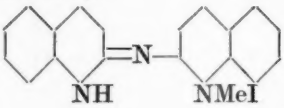
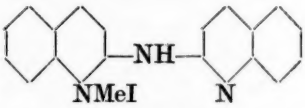
To synthesise the azocyanines, the 2- and 4-aminoquinolines themselves were made the starting point and they were prepared from quinaldinic and cinchonic acids, respectively. Thus methyl quinaldinate was converted into quinaldinamide by the method of Besthorn and Ibele (*Ber.*, 1906, **39**, 2329), who mention that the action of potassium hypobromite yields 2-aminoquinoline; in the absence of the promised details, a satisfactory process was worked out. Cinchonic acid was prepared by the synthesis of Kaufmann and his collaborators from quinoline dimethosulphate (see *Ber.*, 1918, **51**, 116, where the earlier references are given). But there is a gap in these directions, since there is no account of the hydrolysis of 4-cyanoquinoline to cinchonic acid and, according to H. Meyer, 4-cyanoquinoline is remarkable for its stability to saponification (*Monatsh.*, 1902, **23**, 897). It was now found that 4-cyanoquinoline may conveniently be hydrolysed with sulphuric acid in open vessels.

By heating 2-aminoquinoline with 2-chloroquinoline, the hydrochloride of 2 : 2′-diquinolylamine (V) was obtained, but 4-aminoquinoline is less reactive and does not behave similarly. 2 : 2′-Diquinolylamine exists in two modifications, either of which can be obtained at will. The more soluble melts at 151—154° and on heating it is changed into that which melts at 170°. The behaviour on heating is parallel to that of benzylidenediquinaldine (Hamer, J., 1923, **123**, 246). In both cases, the theory postulated by Scheibe (*Ber.*, 1921, **54**, 786) to explain the dimorphism of diquinolylmethane may be applied and the second form of 2 : 2′-diquinolylamine may be represented by VI.

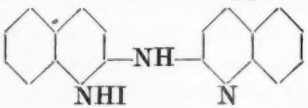
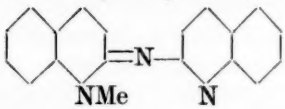
(V.)   (VI.)

Diepolder (*J. pr. Chem.*, 1923, [ii], **106**, 41) prepared 2 : 2′-diquinolylamine but did not observe its dimorphism, simply recording

that it melts about 161°. He states that on heating the base with excess of methyl iodide its monomethiodide is obtained; when this is heated with alkali it loses, not hydriodic acid, but methyl iodide, so that the original diquinolylamine is regenerated. To account for this anomalous behaviour, he suggests that the methiodide should be represented by (VII) instead of by the normal formula (VIII).

(VII.)  (VIII.) 

The correct interpretation of the phenomena is in reality quite different. It is true that analyses of the product formed by the action of methyl iodide on 2 : 2′-diquinolylamine indicate the formula $C_{19}H_{16}N_3I$, corresponding with the monomethiodide, but more careful examination shows it to consist of a mixture of two iodides, $C_{18}H_{14}N_3I$ and $C_{20}H_{18}N_3I$, which must be present in equimolecular proportions. Of these, the first is 2 : 2′-diquinolylamine hydriodide (IX), as was confirmed by the action of sodium hydroxide, which liberated diquinolylamine. The formula $C_{20}H_{18}N_3I$ corresponds with the azocyanine II, which is the methiodide of 1-methyldihydroquinolenyl-2-quinolyl-2′-imine. To explain the formation of this salt, it must be supposed that 2 : 2′-diquinolylamine mono-

(IX.)   (X.)

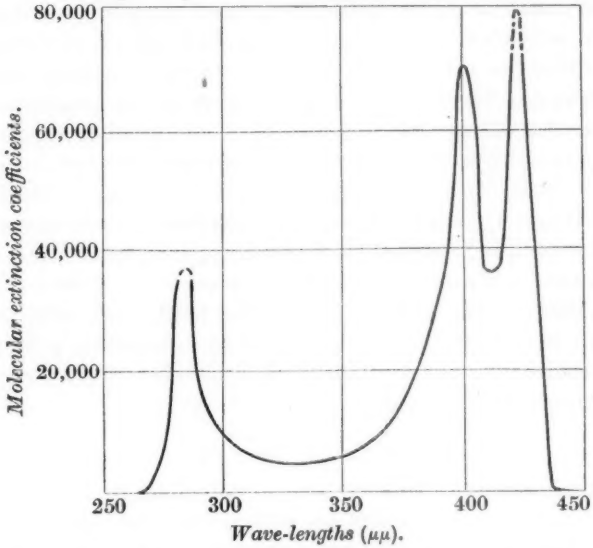
methiodide (VIII) is first produced, but it readily splits off hydrogen iodide, which unites with another molecule of diquinolylamine to form the hydriodide (IX). By elimination of hydrogen iodide, 1-methyldihydroquinolenyl-2-quinolyl-2′-imine (X) is left and in presence of excess of methyl iodide it forms its monomethiodide (II). The substance $C_{20}H_{18}N_3I$ was shown to be identical with 1 : 1′-dimethyl-2 : 2′-azocyanine iodide, prepared as described below.

The acetyl derivative of 2 : 2′-diquinolylamine was prepared and was converted into its dimethosulphate and monomethiodide; by the action of sodium hydroxide on this quaternary sulphate, a 54 per cent. yield of 1-methyldihydroquinolenyl-2-quinolyl-2′-imine (X) was isolated. On treating this base with hydriodic acid, 2 : 2′-diquinolylamine methiodide is formed. Hydrochloric acid gives the corresponding methochloride. In view of Diepolder's statements, it is noteworthy that this true methiodide of 2 : 2′-diquinolylamine is smoothly converted by alkali into 1-methyldihydroquinolenyl-2-quinolyl-2′-imine.

1 : 1′-Dimethyl-2 : 2′-azocyanine iodide, the methiodide of this base, consists of a mixture of orange and yellow crystals. On heating, various colour changes occur, after which both forms melt together; they have the same absorption spectra. This may be a case of geometrical isomerism, since each modification on recrystallisation yields chiefly crystals of its own kind, indicating that the dimorphism corresponds with a difference in molecular constitution.

FIG. 1.

Absorption of 1 : 1′-*dimethyl*-2 : 2′-*azocyanine iodide.*



1 : 1′-Dimethyl-2 : 2′-azocyanine iodide is interesting on account of its relationship to the cyanines. The analogous 1 : 1′-dimethylpseudo*iso*cyanine iodide is a red dye (Fischer and Scheibe, *J. pr. Chem.*, 1919, [ii], **100**, 86); König found that the most intense absorption band lies at 5230, the second at 4880, and the weakest at 4550 (*Ber.*, 1922, **55**, 3293). A solution of 1 : 1′-dimethyl-2 : 2′-azocyanine iodide is, on the other hand, pale yellow with a blue fluorescence and is unlike the cyanines in that it is not decolorised by acids, whilst it has no action on a photographic plate. As shown in the figure, it possesses three absorption bands, of which the strongest is at 4240, the next at 4020, and the weakest at 2850, and these bands are remarkable for their extreme narrowness. It is apparent, then, that the replacement of ·CH· by ·N· has caused a shift of the bands towards the more refrangible region of the spectrum.

Now in passing from the diphenylcarbinol series to the indamines, the substitution of :N· for :CH· causes the bands to be displaced in the opposite direction, since, according to Moir, the factor for such a change is 1·2 (*Trans. Roy. Soc. S. Africa*, 1920, **8**, 303). In this connexion, it seemed of interest to examine other pairs of the same kind, such as *p*-dimethylaminobenzylidenequinaldine ethiodide (König and Treichel, *J. pr. Chem.*, 1921, [ii], **102**, 63), and the *p*-dimethylaminoanil of quinaldinaldehyde ethiodide (Kaufmann and Vallette, *Ber.*, 1912, **45**, 1736). Mr. R. Raper, of Caius College, kindly gave me specimens of these and also of a pair of new compounds prepared by him: *p*-dimethylaminobenzylidene-β-naphthaquinaldine ethiodide and the *p*-dimethylaminoanil of β-naphthaquinaldinaldehyde ethiodide. Each of these possessed one very broad absorption band in the visible region of the spectrum. Replacement of :CH· by :N· had the effect of broadening the band, decreasing its intensity, and shifting it towards the red.

With the last four compounds it was found that, if the linking is by a :CH· group, the substance is a photographic sensitiser, but if by a :N· atom, it possesses desensitising properties. This rule is general in that a similar observation was made by Mills and Smith (J., 1922, **121**, 2724) and by Smith (J., 1923, **123**, 2288) in the case of four pairs of substances prepared by condensing *p*-dimethylaminobenzaldehyde and *p*-nitrosodimethylaniline respectively with various thiazole derivatives.

Experimental.

4-Cyanoquinoline, prepared from quinoline by Kaufmann's method (*loc. cit.*), was purified by dissolving it in dilute sulphuric acid and precipitation from the filtrate with ammonia. The recrystallised substance, instead of melting at 95° as found by H. Meyer (*loc. cit.*), became sticky at 101° and melted at 103—104° (Found: N = 17·87. Calc. for $C_{10}H_6N_2$, N = 18·18 per cent.).

4-Cyanoquinoline (10 grams) was hydrolysed with boiling 70 per cent. sulphuric acid (20 c.c.) for 1 hour, the solution was cooled, diluted, and made alkaline with ammonia, the excess of ammonia expelled, the hot liquid treated with copper acetate, and the copper cinchonate decomposed with hydrogen sulphide; the yield of recrystallised cinchonic acid, m. p. 252°, was 76 per cent.

Methyl cinchonate (yield 84 per cent.) was obtained from methyl alcohol and the acid (compare Mills and Hamer, J., 1922, **121**, 2008).

The method of preparing cinchonamide was similar to that for quinaldinamide, and though the yield of recrystallised cinchon-

amide, m. p. 179—180°, was only 62 per cent., the process was more convenient than that of Wenzel (*Monatsh.*, 1894, **15**, 453).

Wenzel's method for the preparation of 4-aminoquinoline (*loc. cit.*) was modified, cinchonamide being added to potassium hypobromite solution cooled with ice; under these conditions, none of the by-product was formed.

4-Aminoquinoline methiodide was prepared by heating 4-aminoquinoline (1·5 grams) and methyl iodide (1 c.c.) in a sealed tube at 100° for 40 hours, extracting the product with ether, and recrystallising it four times from absolute alcohol; m. p. 228° with previous softening. Claus and Frobenius give m. p. 224° (*J. pr. Chem.*, 1897, [ii], **56**, 181) (Found : I = 44·29. Calc. for $C_{10}H_{11}NI$, I = 44·37 per cent.).

2-Aminoquinoline.—A solution (100 c.c.) of potassium hypobromite, prepared from 8 grams of caustic potash (5 mols.) and 4·65 grams of bromine (1 mol.), was cooled with ice and stirred mechanically while 5 grams of quinaldinamide (1 mol.), ground to a paste with water (25 c.c.), were gradually added; the temperature was slowly raised, and the mixture boiled for 10 minutes. The base, which separated on cooling, was dried in the steam-oven, and recrystallised from hot water, benzene, or dilute alcohol (yield 76 per cent.); m. p. 127—128°. A specimen, which had been three times recrystallised from water and dried in a vacuum desiccator, on heating became sticky at 129° and melted at 131·5° (Found : N = 19·23. Calc. for $C_9H_8N_2$, N = 19·44 per cent.).

2 : 2′-Diquinolylamine (Formulæ V and VI).—2-Aminoquinoline (4 grams; 1 mol.) and 2-chloroquinoline (5 grams; 1·1 mols.) were heated in a sealed tube at 240—260° for 8 hours, when crystals of 2 : 2′-diquinolylamine hydrochloride formed. The base, liberated with boiling 10 per cent. sodium hydroxide, was washed, dried, and extracted with ether. The residue was again treated with alkali, etc., until only a small amount of black material remained. The base from the ether was recrystallised from alcohol; yield 60 per cent. (Found : C = 79·49; H = 4·96; N = 15·57. $C_{18}H_{13}N_3$ requires C = 79·67; H = 4·83; N = 15·50 per cent.).

2 : 2′-Diquinolylamine is easily soluble in benzene, ether, or chloroform, but insoluble in water. The solution in hot alcohol often yielded two kinds of crystals : (*a*) straw-coloured needles, melting at 151—154° to a cloudy drop which clears at 168—169°; if the temperature is very slowly raised, the substance may resolidify about 159° and melt again at 170°; (*b*) compact, orange crystals, m. p. 170°. Conversion of (*a*) into (*b*) occurs without change in weight on heating at 140—150°. The former modifica-

tion is the more soluble and its crystallisation is favoured when concentrated solutions are quickly cooled.

2 : 2′-*Diquinolylamine monohydrochloride*, a bright yellow salt, is very sparingly soluble in dilute hydrochloric acid, water, or alcohol, but much more soluble in strong acid. Its aqueous solution is neutral to litmus. On heating, it remains unmelted at 300°. For analysis it was dried in a vacuum at 60—70° (Found: Cl = 11·62. $C_{18}H_{13}N_3$,HCl requires Cl = 11·53 per cent.). The *monohydriodide*, one of the products of the action of methyl iodide on 2 : 2′-diquinolylamine, is very slightly soluble in alcohol or water and forms small, pale yellow crystals, which remain unmelted at 300°. The *dinitrate* was prepared by dissolving the base in hot nitric acid and recrystallising from nitric acid the very fine needles which separated. The pale yellow product, m. p. about 240° with subsequent violent decomp., was dried in a vacuum at 90—100° (Found: N = 17·74. $C_{18}H_{13}N_3$,2HNO_3 requires N = 17·64 per cent.). The *sulphate* is much more soluble in dilute acid than are the nitrate, hydrochloride, and hydriodide.

Action of Methyl Iodide on 2 : 2′-*Diquinolylamine*.—2 : 2′-Diquinolylamine (3 grams; 1 mol.) and methyl iodide (1·2 c.c.; 1·5 mols.) were heated in a sealed tube at 100° for 48 hours. The powdered solid was extracted with ether, and the undissolved residue (4·2 grams) dried in a vacuum at 70—80° (Found: C = 55·04; H = 3·82; N = 10·00; I = 30·75. $C_{19}H_{16}N_3I$ requires C = 55·18; H = 3·90; N = 10·17; I = 30·72 per cent.). On heating, blackening began at 240—245° and the melting point was about 260—278°. The product, which was a mixture of two compounds, was boiled (3 grams) with insufficient alcohol for complete solution (30 c.c.); the mixture was filtered hot, and the solid again boiled with spirit (30 c.c.). The undissolved residue (1·2 grams) was recrystallised and dried in a vacuum at 70—85°, when analysis showed it to be diquinolylamine monohydriodide (Found: C = 53·62; H = 3·66; N = 10·59; I = 31·63. $C_{18}H_{13}N_3$,HI requires C = 54·14; H = 3·54; N = 10·53; I = 31·81 per cent.); it was converted into diquinolylamine by treatment with alkali. Practically nothing separated from the second filtrate. The crystals (1·2 grams) from the first filtrate were recrystallised twice and dried in a vacuum at 90—100° until of constant weight (Found: C = 56·21; H = 4·23; N = 10·04; I = 29·66. $C_{20}H_{18}N_3I$ requires C = 56·20; H = 4·25; N = 9·84; I = 29·71 per cent.). This iodide is identical with 1-methyldihydroquinolenyl-2-quinolyl-2′-imine methiodide (see below). Both salts, as well as their mixture, melted at 278°; the absorption spectra were identical.

Acetyl-2 : 2′-diquinolylamine.—2 : 2′-Diquinolylamine (4 grams) was boiled for 4 hours with fused sodium acetate (16 grams) and acetic anhydride (80 c.c.), the hot mixture was poured into ice-water and made alkaline with ammonia, and the acetyl derivative recrystallised from spirit, from which it separated in long, almost colourless needles, m. p. 192—193° (yield 74 per cent.) (Found : C = 76·68; H = 4·81; N = 13·26. $C_{20}H_{15}ON_3$ requires C = 76·63; H = 4·83; N = 13·42 per cent.).

Acetyl-2 : 2′-diquinolylamine Dimethosulphate.—The base (3·8 grams) was heated with excess of methyl sulphate (2·5 c.c.) at 120—130° for 15 minutes. The oil was washed with ether, crystallised from hot dilute sulphuric acid and from spirit, and dried on the water-bath (3·2 grams). For analysis, a specimen was recrystallised twice more and was dried in a vacuum at 80—90° (Found : C = 59·91; H = 4·67. $C_{22}H_{21}O_5N_3S$ requires C = 60·08; H = 4·82 per cent.). Its melting point is indefinite and is dependent on the rate of heating. The sulphate is stable towards hydrolysis by concentrated hydrochloric acid or 70 per cent. sulphuric acid.

Acetyl-2 : 2′-diquinolylamine Monomethiodide.—The quaternary sulphate from 3 grams of base was dissolved in hot water and treated with aqueous potassium iodide (8 grams). The orange solid after recrystallisation from alcohol weighed 2·6 grams. For analysis, it was dried in a vacuum at 60—70° (Found : I = 28·04. $C_{21}H_{18}ON_3I$ requires I = 27·89 per cent.). When heated, the iodide becomes sticky about 170° and melts about 260°. It is more soluble in alcohol than in water, is easily soluble in chloroform, slightly soluble in benzene, and insoluble in ether.

1-*Methyldihydroquinolenyl-2-quinolyl-2′-imine* (Formula X).—A solution of recrystallised acetyl-2 : 2′-diquinolylamine dimethosulphate (1 gram) in hot, very dilute sulphuric acid was poured into excess of ice-cold 10 per cent. sodium hydroxide solution. The mixture was diluted and the solid was filtered, washed, and dried. This crude product (0·49 gram) was freed from a little insoluble matter (0·04 gram) with ether, and pure base (0·35 gram), m. p. 116°, obtained from the extract. For analysis, a specimen was recrystallised from dilute alcohol and dried in the steam-oven (Found : C = 79·80; H = 5·25; N = 14·94. $C_{19}H_{15}N_3$ requires C = 79·95; H = 5·30; N = 14·74 per cent.). The base separates from light petroleum in canary-yellow crystals.

2 : 2′-*Diquinolylamine Methiodide.*—A hot alcoholic solution of 1-methyldihydroquinolenyl-2-quinolyl-2′-imine was acidified with hydriodic acid, the yellow, crystalline iodide was washed with alcohol and ether, and dried in a vacuum at 80—90° (Found :

C = 55·18; H = 3·94; N = 10·13; I = 30·63. $C_{19}H_{16}N_3I$ requires C = 55·18; H = 3·90; N = 10·17; I = 30·72 per cent.). The melting point is indefinite and depends on the rate of heating. The iodide is partly blackened on recrystallisation from water or even from absolute alcohol.

A filtered solution of 2 : 2′-diquinolylamine methiodide (0·4 gram) in hot, very dilute sulphuric acid was added to excess of ice-cold 10 per cent. caustic soda. The precipitate was completely dissolved by ether and from the dried extract there was obtained 1-methyldihydroquinolenyl-2-quinolyl-2′-imine (0·2 gram), m. p. 114—116°. Moreover, when the solid methiodide was shaken with soda and ether, all insoluble matter soon disappeared.

2 : 2′-*Diquinolylamine methochloride* was obtained by the action of concentrated hydrochloric acid on a hot alcoholic solution of 1-methyldihydroquinolenyl-2-quinolyl-2′-imine. The pale yellow, crystalline product was dried in a vacuum at 60° (Found: Cl = 11·17. $C_{19}H_{16}N_3Cl$ requires Cl = 11·03 per cent.). The melting point depends on the rate of heating and is about 110—125°. The methochloride can be crystallised from hot water, but is considerably more soluble in alcohol, and fairly soluble in chloroform.

1 : 1′-*Dimethyl*-2 : 2′-*azocyanine Iodide* (Formula II).—1-Methyldihydroquinolenyl-2-quinolyl-2′-imine (0·5 gram) was heated with excess of methyl iodide (1 c.c.) in a sealed tube at 100° for 24 hours. The resulting solid was washed with ether, recrystallised from rectified spirit, in which it was not very soluble, and was dried (0·6 gram) in a vacuum at 90—100° (Found: C = 55·85; H = 4·17; N = 9·88; I = 29·45. $C_{20}H_{18}N_3I$ requires C = 56·20; H = 4·25; N = 9·84; I = 29·71 per cent.). A mixture of yellow crystals with orange crystals showing a blue reflex was generally obtained. When heated, the orange form became yellower at about 140°, but subsequently darkened, and both forms melted simultaneously at 278—285°; decomposition only commenced a couple of degrees lower and the melting point was sharp but dependent on the rate of heating. The two forms have identical absorption spectra. These were photographed by means of a Hilger spectrometer which, instead of the usual sector wheel, was fitted with an adjustment similar to that of the Nutting photometer. There are three very narrow bands, of which the strongest has its maximum at $\lambda = 4240$, where the molecular extinction coefficient $e = 80{,}000$; the crest of the next is at 4020, where $e = 70{,}000$; the weakest band lies at 2850, where $e = 40{,}000$.

I was enabled to carry out the crystallographic investigation of the yellow form of 1 : 1′-dimethyl-2 : 2′-azocyanine iodide through

the kindness of Dr. A. Hutchinson, to whom I am deeply indebted for his instruction and help.

Crystal system : monoclinic. Class : holohedral. Axial ratio : $a : b : c = 1{\cdot}897 : 1 : 1{\cdot}0913$. Axial angle : $\beta = 129° 8'$.

Table of Angles.

Angle measured.	No. of measurements.	Limits.	Mean. Obs.	Mean. Calc.
Am = (100) : (110)	4	55° 41½′—55° 56′	55° 48½′	*
Ac = (100) : (001)	4	50 41½—50 58½	50 52	50° 52′
Cq = (001) : (011)	3	40 0½—40 39	40 15	*
Cm = (001) : (110)	8	68 53½—69 42	69 13	*
Qm = (011) : (110)	1	36 22	36 22	36 22½

Habit : Flat tabular on *c*{001}. The crystals were extremely small, but fairly well developed.

p-*Dimethylaminobenzylidenequinaldine Ethiodide.*—By means of a Nutting photometer, the absorption in the visible region of the spectrum was examined and it was found that there is one band with its crest at 5320, where $\epsilon = 56{,}000$. The substance has a very feeble sensitising action, which extends to 6700 for moderate exposures.

p-*Dimethylaminoanil of Quinaldinaldehyde Ethiodide.*—This compound, like the former, has one band in the visible region, but it is broader and less intense. The crest lies at 5680, where $\epsilon = 39{,}000$. Towards an Ilford special rapid plate, the ethiodide has a more powerful desensitising action than has safranine.

p-*Dimethylaminobenzylidene-β-naphthaquinaldine Ethiodide.*—The broad absorption band has its crest at 5250, where $\epsilon = 57{,}500$. The substance is a good sensitiser, showing a very uniform band which extends to 6900.

p-*Dimethylaminoanil of β-naphthaquinaldinaldehyde Ethiodide.*—The absorption band is broader and less intense than that of the preceding compound; its maximum lies at 5600, where ϵ is 41,000. The substance possesses a desensitising action which is not nearly so powerful as that of the *p*-dimethylaminoanil of quinaldinaldehyde ethiodide.

I wish to express my thanks to Dr. W. H. Mills for the interest he has taken in this work.

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CLXXI.—*The Hydrolysis of Potassium Ferricyanide and Potassium Cobalticyanide by Sulphuric Acid.*

By HENRY BASSETT and ALEXANDER STEVEN CORBET.

I. *Potassium Ferricyanide.*

THE hydrolysis of potassium ferrocyanide by dilute and by concentrated sulphuric acid follows the equations:

$$2K_4Fe(CN)_6 + 3H_2SO_4 = 3K_2SO_4 + K_2Fe[Fe(CN)_6] + 6HCN$$

$$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + 3(NH_4)_2SO_4 + FeSO_4 + 6CO,$$

and in text-books it is presumed that similar reactions take place in the case of potassium ferricyanide:

$$2K_3Fe(CN)_6 + 6H_2SO_4 = 3K_2SO_4 + Fe_2(SO_4)_3 + 12HCN$$

$$2K_3Fe(CN)_6 + 12H_2SO_4 + 12H_2O = 3K_2SO_4 + 6(NH_4)_2SO_4 + Fe_2(SO_4)_3 + 12CO.$$

Little attention appears to have been directed to the latter reactions, and apparently Williamson (*Annalen*, 1846, **57**, 243) was the only chemist to give the subject any serious consideration. His work, however, was chiefly concerned with the ultimate analysis of the complex cyanides of iron, and the action of concentrated sulphuric acid on potassium ferricyanide was studied only in a qualitative manner. The fact that carbon dioxide appears as an end-product in the reaction apparently escaped observation entirely.

In the present investigation, a series of experiments was carried out in which potassium ferricyanide was warmed with sulphuric acid of varying concentrations and the proportions of the end-products obtained were quantitatively determined.

On first warming the ferricyanide with concentrated sulphuric acid a greenish-white precipitate was obtained, the colour of which varied considerably with the concentration of the acid. The nature of this precipitate was not investigated, but presumably it was hydroferricyanic acid or an acid salt of that compound. On further warming, the precipitate turned slightly blue and eventually disappeared, a clear yellowish-green solution being produced. The time of heating required for this change increased as the concentration of the sulphuric acid used was diminished. It was at the stage in the reaction when the solution was clearing that the greater part of the carbon monoxide was evolved.

We have found that when potassium ferricyanide is hydrolysed with excess of sulphuric acid some ferrous salt is invariably formed.

Using 90 per cent. (by weight) sulphuric acid, the hydrolysis could

not be completed, but with about 80 per cent. sulphuric acid almost the whole of the ferric salt was reduced, whilst one-twelfth of the carbon monoxide was oxidised to carbon dioxide. In this case, the completed reaction was represented by the equation

$$2K_3Fe(CN)_6 + 11H_2SO_4 + 13H_2O = 3K_2SO_4 + 6(NH_4)_2SO_4 + 2FeSO_4 + 11CO + CO_2.$$

On using more dilute sulphuric acid, a diminution in the yield of oxides of carbon and ferrous sulphate resulted, with a corresponding increase in the hydrocyanic acid and ferric sulphate formed. In fact, the reaction tended more and more to follow the equation

$$2K_3Fe(CN)_6 + 6H_2SO_4 = 3K_2SO_4 + Fe_2(SO_4)_3 + 12HCN.$$

When the concentration of the sulphuric acid was not above 30 per cent., the hydrolysis took much longer than previously, and the carbon finally appeared almost wholly as hydrocyanic acid. With acid of this concentration, a yellowish-green solution was obtained which persisted for some time, eventually turning very dark and finally clearing to give a straw-coloured solution. At this stage, the oxides of carbon were evolved in such small amounts that determinations were scarcely practicable.

With any given concentration of sulphuric acid, the proportions of the end-products were not quite constant, but appeared to depend to some extent on the manner in which the mixture was heated. This was to be expected, as in all cases water distilled over, causing the acid solution to become more concentrated as heating was continued.

In general, the course of the reaction appears to be similar to that between potassium ferrocyanide and sulphuric acid. The hydroferricyanic acid (or acid salt) first liberated is hydrolysed to potassium sulphate, ferric sulphate, and hydrocyanic acid, and in presence of dilute acid the reaction goes no farther and hydrocyanic acid distils over. With more concentrated acid, however, some or all of the hydrocyanic acid is converted into formic acid and ultimately carbon monoxide. Some or all of the ferric salt is reduced by the formic acid with formation of a corresponding amount of carbon dioxide, and the extent to which this occurs depends on the concentration of the sulphuric acid.

That the formic acid is the reducing agent appears probable from experiments in which ferric alum and formic acid were heated together in presence of sulphuric acid in quantities which made the conditions comparable with those of the reaction under consideration. In these experiments, it was found that the formic acid was able to reduce the ferric salt present.

Under conditions which prevailed during the experiments, carbon monoxide had no reducing action on ferric salts in presence of sulphuric acid.

It is well known that aqueous solutions of potassium ferricyanide decompose comparatively quickly when exposed to light and Vogel (*Ber.*, 1871, **4**, 90) first showed that the formation of ferrocyanide in solutions of ferricyanide on standing is due to the action of light and not to dust particles. The nature of this photochemical change, however, does not appear to have been fully investigated. Some reduction of ferric to ferrous iron certainly occurs which leads to the formation of blue complex ferri-ferrocyanides, but it seems more than doubtful whether the reduction mechanism is the same as that operating under the conditions we have examined. In the light reaction, it may well be that ferric ions oxidise cyanide ions to cyanogen in spite of the fact that there is only a very low concentration of either of these ions in a solution of potassium ferricyanide. The reaction would then be analogous to the oxidation of cyanide by cupric or thallic salts and the possibility of this same mechanism prevailing during the hydrolysis of potassium ferricyanide by sulphuric acid is not entirely excluded. It seems incapable of proof, however, and unlikely from the fact that the proportion of ferric ions reduced increased with the concentration of the acid. Concentrated acid solutions would not be favourable to the existence of cyanide-ions owing to hydrocyanic acid being so weak.

Experimental.

The purity of the potassium ferricyanide used could not be accurately ascertained by means of potassium permanganate, and was eventually determined by Müller and Diefenthäler's modification of Lenssen's method (*Annalen*, 1854, **91**, 240). The faintly acid solution of the ferricyanide was treated with potassium iodide and pure zinc sulphate; iodine was liberated, whilst the ferrocyanide formed was precipitated as zinc ferrocyanide. The free iodine was titrated against sodium thiosulphate, with starch as indicator. The material was thus found to contain 99·6 per cent. of potassium ferricyanide. The purity was further checked by a determination of the total nitrogen present as hydrocyanic acid and ammonia after hydrolysis.

For each experiment, about 0·05 to 0·1 gram of potassium ferricyanide was weighed into a distilling flask, which was connected with a Schiff's nitrometer containing strong potassium hydroxide solution, prepared from boiled water and saturated with carbon monoxide before use (carbon monoxide was sufficiently soluble in

strong potassium hydroxide solution to affect the results). Dry carbon dioxide from a Farmer apparatus (J., 1920, **117**, 1446) was used to displace the air and to drive over any carbon monoxide remaining in the distilling flask on the completion of the hydrolysis. The sulphuric acid used for the experiments was boiled to expel air, cooled in a current of carbon dioxide, and introduced into the flask by means of a tap-funnel. (The strength of the sulphuric acid was first determined by titration with standard alkali, but later it was found that hydrometers were sufficiently accurate for the purpose.) The mixture was heated to boiling while the current of carbon dioxide carried the carbon monoxide evolved to the nitrometer. On completion of the hydrolysis the carbon dioxide was passed for some time to ensure all the carbon monoxide being collected.

The residual solution in the distilling flask was diluted and the ferrous salt present titrated with 0·1*N*-potassium permanganate solution. This incidentally gave the carbon monoxide oxidised to dioxide. After the titration, the same solution was used to estimate the ammonia present (Kjeldahl's method).

It was found to be advisable to estimate the hydrocyanic acid and carbon dioxide in separate experiments. For determinations of the hydrocyanic acid, the aqueous distillate was absorbed in dilute potassium hydroxide contained in a flask interposed between the distilling flask and nitrometer. After hydrolysis, the contents of the flask were titrated against 0·1*N*-silver nitrate.

Some difficulty was experienced in the direct estimation of the carbon dioxide. In this case, the hydrolysis with sulphuric acid was carried out in a current of dry, carbon dioxide-free air, and any carbon dioxide formed was absorbed in 0·1*N*-sodium hydroxide solution contained in a series of boiling tubes. On completion of the hydrolysis, 10 c.c. of barium chloride solution were added to each of the tubes and the contents were titrated against standard acid with phenolphthalein as indicator.

The difficulty of this estimation lay in the fact that only a small amount of carbon dioxide was obtained with dilute sulphuric acid, but when the maximum yield was obtained with concentrated sulphuric acid there was the danger of acid coming over in the distillate at the close of the hydrolysis. However, with care, it was possible to prevent this and show that the amount of carbon dioxide obtained was the same as that calculated from the permanganate titrations of the ferrous salt.

The results obtained are given in the table and plotted in the diagram.

Diagram showing the distribution of carbon atoms after hydrolysis of two molecules of potassium ferricyanide (full lines) and potassium cobalticyanide (dotted lines) by sulphuric acid.

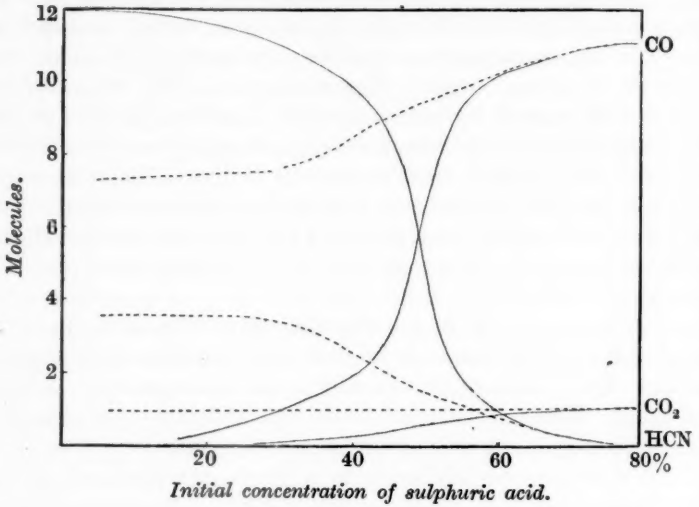


Table Showing Distribution of Carbon Atoms after Hydrolysis of 2 Mols. of Potassium Ferricyanide.

Initial conc. of H_2SO_4 %.	CO (mols.).	CO_2(KMnO$_4$) (mols.).	HCN (mols.).	Initial conc. of H_2SO_4 %.	CO (mols.).	CO_2(KMnO$_4$) (mols.).	HCN (mols.).
9·47		0·09	11·94	60	9·54	0·85	
18·96		0·05	11·68	,,	9·96	0·86	
29·21		0·04	11·08	,,	10·19	0·88	
,,		0·05	11·26	,,	10·33	0·79	
30·48			11·11	,,	10·46	0·79	
30·77	0·59	0·12		61·35			0·41
39·85	0·91	0·18	9·89	,,			0·48
,,	1·39	0·21	9·83	63·85		0·89	
40·06			10·69	67·59			1·71
46·94	5·51			70	10·34	0·85	
48			5·11	,,	10·61	0·92	
49·96	6·56	0·62		,,	10·62	0·83	
,,	6·99	0·66		70·67	10·67	0·91	
50		0·58		71·10	10·01	0·79	
,,		0·59		77·6		0·93	
56·38	8·39		3·56	,, *		0·94	
58·28			0·75	80	10·71	1·12	
,,			0·97	,,	10·88	0·91	
,,			0·98	,,	11·12	1·01	
60	9·12	0·71		81·56		0·90	
,,	9·32	0·81					

Initial conc. of H_2SO_4 %	71·16	71·16	72·6	77·6*
Mols. of CO_2 (direct)	0·84	1·03	0·75	0·94

II. *Potassium Cobalticyanide.*

The action of sulphuric acid on potassium cobalticyanide was described by Gmelin, who first prepared it ("Handbook of Chemistry," 1852, VII, 493). His observations, however, were of a purely qualitative nature, and he did not record that carbon monoxide and carbon dioxide are among the products of hydrolysis.

It was anticipated that the decomposition of potassium cobalticyanide by sulphuric acid would differ from that of potassium ferricyanide only in that a constant amount of carbon dioxide would be evolved, irrespective of the concentration of the sulphuric acid used. This should follow from the fact that all the cobalt present would appear finally as cobalt*ous* sulphate. It was found, however, that the complete decomposition of the cobalticyanide was much more difficult to achieve than that of the ferricyanide.

When the cobalticyanide was first warmed with sulphuric acid of initial concentration about 80 per cent. (by weight), a white precipitate was thrown down, which, presumably, was hydrocobalticyanic acid; further warming gave a pink turbid solution which eventually cleared. With acid of this initial concentration, scarcely any hydrocyanic acid was obtained and the reaction followed the equation

$$2K_3Co(CN)_6 + 11H_2SO_4 + 13H_2O = 3K_2SO_4 + 6(NH_4)_2SO_4 + 2CoSO_4 + 11CO + CO_2$$

in analogy with the ferricyanide hydrolysis by sulphuric acid of this concentration. On using more dilute sulphuric acid for the hydrolysis, the same colour changes were observed, but hydrocyanic acid began to appear among the end-products in increasing amount. After heating for a short time with sulphuric acid of concentration not above 30 per cent., a bright yellow solution was obtained which became turbid on further warming, but finally cleared to give a pink solution. When the initial concentration of the acid was below 30 per cent. the proportions of the end-products were practically constant, but only about one-third of the theoretical yield of hydrocyanic acid was obtained.

It was thought that this might be due to the fact that potassium cobalticyanide is more stable than the corresponding ferricyanide, and therefore a longer time is required for complete decomposition. Under the conditions prevailing during the experiments, water distilled over during the warming and the acid became more and more concentrated. The cobalticyanide being only slowly decomposed by the dilute acid, the latter became concentrated before the decomposition was more than about one-third completed, and so the cobalticyanide was eventually hydrolysed by concentrated acid.

To test this view, an experiment was carried out in which potassium cobalticyanide was hydrolysed by 29·84 per cent. sulphuric acid, and the mixture distilled under reflux until hydrocyanic acid ceased to be evolved. The solution became lemon-yellow on first warming, but straw-coloured as hydrolysis proceeded. It was not possible to complete the hydrolysis in one heating, but the experiment was continued for varying periods for four days, during which the hydrocyanic acid in the distillate was estimated from time to time by titration with silver nitrate. In this way, nearly $\frac{11}{12}$ of the carbon atoms finally appeared as hydrocyanic acid, showing that under these conditions the reaction tended to follow the equation

$$2K_3Co(CN)_6 + 6H_2SO_4 + 2H_2O = 3K_2SO_4 + 2CoSO_4 + (NH_4)HSO_4 + 11HCN + CO_2.$$

Molecules of Hydrocyanic Acid obtained by Hydrolysis of 2 Mols. of Potassium Cobalticyanide under a Reflux Condenser. Concentration of Sulphuric Acid = 29·84 per cent.

Time (hours)	5·75	8·75	10·75	17·75	20·50	28·75	31·25	35·25
Mols. of HCN.....	6·46	7·20	8·12	9·04	9·59	10·14	10·32	10·32

EXPERIMENTAL.

An attempt was made to determine the purity of the potassium cobalticyanide by Braun's method (*Z. Chem.*, 1866, **2**, 283) of titrating with silver nitrate in presence of potassium chromate, but this did not yield satisfactory results. The purity was found to be 99·24 per cent. by an estimation of the ammonia and hydrocyanic acid produced on decomposition with 47 per cent. sulphuric acid.

The experiments were carried out as in the case of the ferricyanide. The determinations were practically confined to hydrocyanic acid, but a few estimations of carbon dioxide also were made. The results are tabulated and represented graphically, the carbon monoxide being obtained by difference.

Distribution of Carbon Atoms after Hydrolysis of 2 Mols. of Potassium Cobalticyanide. a = initial conc. of sulphuric acid per cent.

a.....	9·80	19·61	19·61	30·48	40·93	50·11	54·55	60·65	70·10	77·6	81·56
HCN mols.	3·40	3·38	3·71	3·48	2·55	1·55		0·92	0·20		
CO_2 mols. ...						0·97				1·11	0·85

It must be emphasised that the figures in the top row give the initial concentration of sulphuric acid. Owing to the slowness of the reaction and distillation of water hydrolysis mostly takes place after considerable concentration has occurred. There is thus no

direct relationship between the hydrocyanic acid produced and the values of *a*.

Potassium Aquopentacyanocobaltiate.

It is probable that the hydrolysis of complex cyanides occurs in a series of relatively simple steps. Some of these may involve replacement of cyanogen groups by H_2O. Some evidence for the intermediate formation of such aquo-compounds in the case of the hydrolysis of potassium cobalticyanide has been obtained. Potassium cobalticyanide was warmed with 30 per cent. sulphuric acid until a deep yellow solution was formed. This was rapidly cooled and neutralised with potassium carbonate. On evaporation in a vacuum and removal of the sulphates, which crystallised first, a white, crystalline substance was finally obtained. Analysis of this gave figures approaching those required by a potassium aquopentacyanocobaltiate $3K_3Co(CN)_6,K_2[Co(CN)_5{\cdot}H_2O]$, similar to the aquopentacyanoferriate obtained by Briggs (J., 1920, **117**, 1026). A similar product was also obtained by the action of bromine on potassium cobalticyanide under conditions such as were employed by Briggs for the ferricyanide.

Summary.

1. Potassium ferricyanide is hydrolysed by concentrated sulphuric acid according to the equation

$$2K_3Fe(CN)_6 + 11H_2SO_4 + 13H_2O = 3K_2SO_4 + 6(NH_4)_2SO_4 + 2FeSO_4 + 11CO + CO_2.$$

The fact that ferrous sulphate and carbon dioxide appear among the end-products has not been observed previously. With more dilute acid, the reaction tends to follow the equation

$$2K_3Fe(CN)_6 + 6H_2SO_4 = 3K_2SO_4 + Fe_2(SO_4)_3 + 12HCN.$$

2. The hydrolysis of potassium cobalticyanide by concentrated sulphuric acid follows the equation

$$2K_3Co(CN)_6 + 11H_2SO_4 + 13H_2O = 3K_2SO_4 + 6(NH_4)_2SO_4 + 2CoSO_4 + 11CO + CO_2.$$

With more dilute acid, hydrocyanic acid is obtained as in the case of ferricyanide, but the hydrolysis is slow owing to the greater stability of the cobalticyanide. By long digestion under reflux the amount of hydrocyanic acid obtained is that required by the equation

$$2K_3Co(CN)_6 + 6H_2SO_4 + 2H_2O = 3K_2SO_4 + 2CoSO_4 + (NH_4)HSO_4 + 11HCN + CO_2.$$

3. A white compound appeared as an intermediate product of hydrolysis, and a white complex cobalticyanide was also obtained by the action of bromine on potassium cobalticyanide. These substances, which appear to be potassium aquopentacyanocobaltiates, were not fully investigated.

UNIVERSITY COLLEGE, READING. [*Received, March 22nd*, 1924.]

CLXXII.—*The Potassium Salts of Phenolphthalein.*

By HENRY BASSETT and DOUGLAS JAMES TALBOT BAGNALL.

AN investigation of the system phenolphthalein–sodium hydroxide–water at 25° (Bassett and Halton, J., 1923, **123**, 1291) showed that various hydrates of the mono-, di-, and tri-sodium salts of phenolphthalein could be obtained as crystalline solids. All were colourless, however, even those in equilibrium with the most highly coloured solutions. This was considered to show, not that a solid red salt did not exist, but that its concentration in aqueous solutions at 25° was never sufficient to enable it to separate in the solid state. Potassium salts are frequently less hydrated and less soluble than the corresponding sodium salts. It is possible, therefore, that conditions might be more favourable for the isolation of a solid red potassium salt of phenolphthalein than for that of the red sodium salt. For this reason, the system phenolphthalein–potassium hydroxide–water has been studied at 25°.

The conditions holding in the potash system seem to be generally very similar to those which prevail in the soda system. No red salt has been obtained as a solid phase, although a number of colourless hydrates of the mono-, di-, and tri-potassium salts of phenolphthalein have been isolated. The results obtained with the potassium compounds are rather less definite than those given by the sodium compounds. This is due to the fact that, although the transition from mono-salt to di- or tri-salt causes a well-marked break in the solubility curve, the curves corresponding to the various hydrates of these salts are practically continuous. For this reason, there are relatively small differences in the stabilities of adjacent hydrates, so that the regions of the several hydrates frequently overlap, and it is not always possible in such cases to say which is the stable compound. Quite the same confidence cannot be felt in the existence of the numerous hydrates indicated by the solubility determinations as when each hydrate corresponds to a sharply differentiated portion of the solubility curve, as was the case with the hydrates of the sodium salts of phenolphthalein.

It is possible at 25° to obtain a solution saturated with respect to the tripotassium salt of phenolphthalein which contains potash and phenolphthalein in the same ratio in which they are present in the solid salt. This is not possible with the mono- or di-potassium salt. The tripotassium salt can actually exist, as tetrahydrate, in contact with a considerable range of solutions in which the ratio potash : phenolphthalein is less than that for the tri-salt. This serves to show how complex must be the equilibria prevailing in these solutions—a matter which was discussed by Bassett and Halton (*loc. cit.*). A tetrahydrate of the tripotassium salt is also found in metastable equilibrium with solutions which are supersaturated with respect to $KOH,2H_2O$, which is the hydrate of potassium hydroxide stable in contact with saturated solution at 25° (Pickering, J., 1893, **63**, 890). It is uncertain whether it is one and the same tetrahydrate or whether there are two different forms. In the former case, we have an interesting example of an equilibrium diagram showing two ends of a solubility curve, the central portion of which is masked by curves belonging to other hydrates. It may be noted that the total water content of the less alkaline solutions in equilibrium with the tetrahydrate is actually less than that of the solutions at the more alkaline end of the system.

There appear to be only three cases where the preparation of crystalline potassium salts of phenolphthalein is mentioned in the literature. Kober and Marshall (*J. Amer. Chem. Soc.*, 1911, **33**, 59, 1779) obtained the pentahydrate of the tripotassium salt in the form of colourless, microscopic plates by evaporating a strong caustic potash solution which had been saturated with phenolphthalein. By the action of carbon dioxide on an alcoholic solution of the tripotassium salt Kober, Marshall, and Rosenfeld (*ibid.*, 1912, **34**, 1424) obtained colourless prisms of a monopotassium salt containing 1 mol. of water and 1 mol. of alcohol of crystallisation.

The claim of Oddo and Vassallo (*Gazzetta*, 1912, **42**, ii, 204) to have obtained a solid red monopotassium salt has already been dealt with (Bassett and Halton, *loc. cit.*). It is possible that Oddo and Vassallo noticed that their original crystals were colourless, for they state "in the powdered condition the crystals are reddish-violet," but they say nothing about the colour before powdering. The colourless crystals obtained by the Italian authors' method soon become pink on exposure to air owing to moisture absorption. We are, however, of the opinion that the sudden deep reddening which occurs on applying pressure to the crystals is due, not to absorption of moisture, but to the formation of red solution owing to partial melting in water or alcohol of crystallisation. The powder

formed is obviously slightly pasty. The transition point, which is thus lowered by pressure, seems to be at about 100° under atmospheric pressure, for, on slowly heating the colourless crystals, partial melting and reddening occur at that temperature. Although no solid red salt could be obtained from aqueous solutions, it seemed possible that it might be formed by suitable treatment of the solid colourless salts. Only limited success attended the experiments made to test this possibility.

The colourless monopotassium salt was obtained in the dry state by maintaining suitable mixtures in the thermostat, with shaking, for a sufficient time, then filtering with suction, washing with several small quantities of absolute alcohol, and drying in a vacuum at the ordinary temperature. So prepared, the salt consisted of very small, irregular, colourless crystals which contained some alcohol as well as water of crystallisation. On addition of water, it gave a red solution and a precipitate of phenolphthalein. When heated in the ordinary way, it partly melted in its water or alcohol of crystallisation at about 100°, forming a deep red, viscous mass. On heating slowly in a vacuum at 130°, a deep red, solid product was obtained without any obvious melting, although the appearance of the red product suggested that partial melting did occur. The dry tripotassium salt could also be obtained in a similar manner to that just indicated. No alcohol seemed to be taken up by the tri-salt during the washing with alcohol, nor did water of crystallisation appear to be lost. Which hydrate was obtained depended on the composition of the aqueous solution. In a number of experiments it was the one expected from an analysis of the solution. The tri-salt consisted of small, colourless, rhomboidal crystals which slowly turned pale pink on exposure to the atmosphere. With water a clear, very pale pink solution was first formed which gradually deepened in colour to red. Some dry crystals of the tri-salt which contained 8 mols. of water of crystallisation showed no signs of melting either when heated in the ordinary way or in a vacuum. On slowly heating at 150° in a vacuum, the almost colourless salt changed to red, then through violet to a very dark brownish-red, remaining as a perfectly dry, loose powder the whole time. If even only very partial melting in water of crystallisation had occurred, the powder would probably have sintered together. When the temperature was raised to 170°, the solid assumed a metallic lustre. After heating to constant weight at 150°, the deep red product contained K_2O 29·1 and phenolphthalein anhydride 61·9, as compared with 29·06 and 61·69 per cent. for a tripotassium salt with 2 mols. of water of crystallisation. In spite of this close agreement, the dark red product of dehydration is not considered

to be such a hydrate. It seems likely that, during the heating, potassium hydroxide has been eliminated with formation of a red quinonoid salt. The latter could be either the dipotassium salt, $CO_2K{\cdot}C_6H_4{\cdot}C(C_6H_4{\cdot}OK){:}C_6H_4{:}O$ or the mono-salt,

$$CO_2K{\cdot}C_6H_4{\cdot}C(C_6H_4{\cdot}OH){:}C_6H_4{:}O,$$

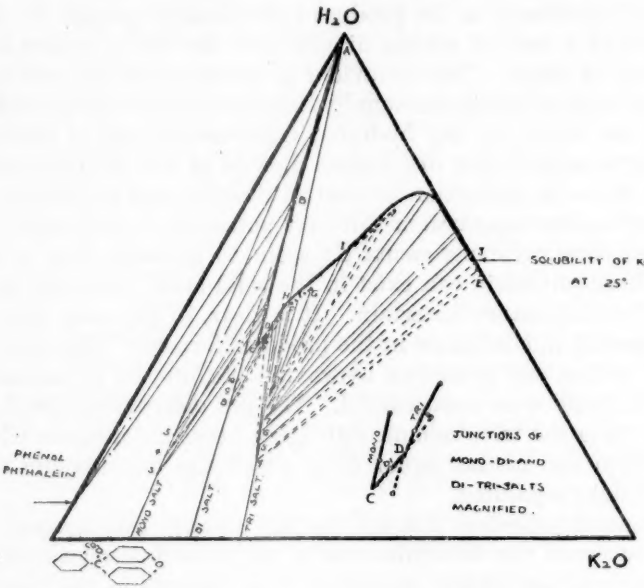
if the second phenolic potassium atom is displaced by the action of water vapour. An equimolecular mixture of the mono-salt and a hydrate, $2KOH,H_2O$, would have the composition found for the red dehydration product. On heating the latter at 100° in a current of dry carbon dioxide until the weight was constant, the colour was not altered. Water had been given off and carbon dioxide absorbed, however, whilst the change of weight and the amount of carbonate in the product corresponded roughly to the absorption of 1 mol. of carbon dioxide and the loss of rather less than 1 mol. of water. This behaviour is, however, no real evidence for the presence of free potassium hydroxide in the red dehydration product, for when the dry hydrated tripotassium salt of phenolphthalein is treated with dry carbon dioxide at the ordinary temperature there is absorption of carbon dioxide and formation of the colourless monopotassium salt and potassium bicarbonate.

The dehydration experiments do seem to indicate that a red salt of phenolphthalein can exist in the solid state, although they leave its precise nature uncertain. It is clear, in any case, that it is only present in admixture in the products formed. Attempts to separate it from any potassium hydroxide also present by means of organic solvents were unsuccessful. The red dehydration product obtained from the tripotassium salt again became colourless when treated with the mother-liquor from which the tripotassium salt had originally separated.

The general procedure followed in the present investigation, so far as concerned the determination of the solubility relationships of the system, was closely similar to that followed in the case of the sodium salts. As a rule, "A.R." stick potash was used in making up the mixtures. This actually contained as impurities about 2 parts of sodium hydroxide and 2 parts of potassium carbonate per 100 parts of potassium hydroxide. It seemed very doubtful whether potash prepared direct from the metal would be much better than this, for the potassium metal at our disposal contained about 1 per cent. of sodium. It was also considered that these small proportions of sodium hydroxide and potassium carbonate would have little effect on the results obtained. A few experiments carried out with potash prepared from the metal by Cornog's method (*J. Amer. Chem. Soc.*, 1921, **43**, 2573) fell into line with those in which A.R. potash was used. In the tables of results,

K_2O really refers to total alkali. These figures were obtained by adding excess of standard acid and titrating the mixture with standard caustic soda, prepared from metal. The excess of acid decomposed the colourless monopotassium salt practically at once, whereas considerable time was required for this if direct titration with acid was attempted. The solids were always examined under the microscope. All were colourless and generally in the form of small, more or less rhomboidal crystals. No characteristic differences in the appearance of different salts or hydrates were noticed.

The experimental results were plotted on the usual triangular diagram and the nature of the several solid phases can be seen from



an inspection of the figure. On this have also been drawn the three lines which pass through all possible mixtures in which the ratio potash : phenolphthalein is the same as in the pure mono-, di-, and tri-potassium salts. Curve *AB* in the diagram corresponds to solutions in equilibrium with solid phenolphthalein. Such solutions contain approximately 2 mols. of caustic potash per mol. of dissolved phenolphthalein. Curve *BC* represents solutions in equilibrium with the monopotassium salts of phenolphthalein. Hydrates with 5, 4, and 3 mols. of water of crystallisation appear to exist, but it is not possible to state the precise limits of their stability. The composition of the equilibrium solution at *B* is approximately 8·0 per cent. K_2O and 24·5 per cent. phenolphthalein

anhydride, whilst that at *C* is 15·5 per cent. K_2O and 45·5 per cent. phenolphthalein anhydride. From *C* to *D* dipotassium salts are the stable solid phases and, again, three hydrates seem to exist, although it is possible that the 9-hydrate is really a mixture of the 10 and 8, as only one point corresponding to it was obtained. *D*, the point at which the tripotassium salt becomes the stable solid phase, corresponds to a solution containing 16·5 per cent. K_2O and 42·0 per cent. phenolphthalein anhydride, but both the di- and tri-salts have been followed for some distance on either side of this point into metastable regions. Solutions in this region are deeply coloured and very viscous. *J* represents the saturated solution of $KOH,2H_2O$ in pure water, which contains 45·3 per cent. K_2O (Pickering, *loc. cit.*). The tripotassium salts have, however, been followed into regions supersaturated with respect to $KOH,2H_2O$, and in this metastable region it is a tetrahydrate which separates. This may or may not be identical with the tetrahydrate which separates from solutions represented by the *DH* portion of the tri-salt curve.

The curve *DHIJE* corresponds to solutions saturated with respect to the various hydrates of the tripotassium salt. These hydrates appear to contain 9, 8, 7, 6, 5, and 4 mols. of water, and there seems to be a second unstable form of the 9-hydrate (curve *FG*). There is a fairly well-marked break at *I* (21·5 per cent. K_2O and 21·0 per cent. phenolphthalein anhydride), where the curves of the 9- and 8-hydrate cut, but the positions of the points where the curves of the other hydrates intersect are undecided.

Table giving the compositions of moist solid and liquid phases in the system phenolphthalein–potassium hydroxide–water at 25°.

Moist solid phase.			Liquid phase.		
K_2O %.	Phenolphthalein anhydride %.	H_2O %.	K_2O %.	Phenolphthalein anhydride %.	H_2O %.
Solid phase : Phenolphthalein. Curve *AB*.					
1·17	74·86	23·97	4·96	13·86	81·18
*1·09	84·55	14·36	7·49	24·20	68·31
Hydrates of monopotassium salts. Curve *BC*.					
Solid phase : Monopotassium salt, $5H_2O$.					
9·51	51·41	39·08	8·25	25·06	66·69
10·23	59·97	29·80	8·97	27·75	63·28
*11·60	50·76	37·64	12·43	38·74	48·83
12·32	48·40	39·28	13·22	39·91	46·87
Solid phase : Monopotassium salt, $4H_2O$.					
9·15	51·22	39·63	11·26	33·60	55·14
13·28	49·40	37·32	14·14	41·59	44·27

Moist solid phase.			Liquid phase.		
K_2O %.	Phenolphthalein anhydride %.	H_2O %.	K_2O %.	Phenolphthalein anhydride %.	H_2O %.
	Solid phase : Monopotassium salt, $3H_2O$.				
12·98	48·00	39·02	13·19	40·34	46·47
14·41	50·61	34·98	15·11	44·31	40·58
	Hydrates of Dipotassium salts. Curve *CD*.				
	Solid phase : Dipotassium salt, $10H_2O$.				
*16·33	51·07	32·60	15·77	45·76	38·47
16·40	51·60	32·00	15·88	44·66	39·46
	Solid phase : Dipotassium salt, $9H_2O$.				
16·64	51·00	32·36	16·44	43·50	40·06
	Solid phase : Dipotassium salt, $8H_2O$.				
17·02	50·70	32·28	15·92	43·80	40·28
17·12	49·02	33·86	16·62	42·62	40·76
17·21	45·53	37·26	17·31	39·01	43·68
	Hydrates of tripotassium salts. Curve *DE*.				
	Solid phase : Tripotassium salt, $4H_2O$.				
20·44	49·00	30·56	17·15	44·90	37·95
20·74	47·13	32·13	16·50	40·74	42·76
20·95	47·01	32·04	16·98	39·22	43·80
22·05	48·15	29·80	16·60	37·06	46·34
	Solid phase : Tripotassium salt, $9H_2O$.				
*20·60	41·76	37·64	17·72	33·24	49·04
22·60	44·10	33·30	19·84	27·47	52·69
22·92	43·65	33·43	21·57	22·11	56·32
	Curve *FG*.				
22·14	46·60	31·26	17·80	35·67	46·53
22·17	45·07	32·76	19·68	30·90	49·42
	Solid phase : Tripotassium salt, $8H_2O$.				
23·42	41·84	34·74	22·21	19·47	58·32
24·70	44·10	31·20	24·74	10·70	64·56
24·35	38·30	37·35	25·64	8·15	66·21
24·20	44·10	31·70	28·27	3·10	68·63
24·54	40·97	34·49	28·98	2·69	68·33
24·55	41·80	33·65	29·50	2·03	68·47
	Solid phase : Tripotassium salt, $7H_2O$.				
24·70	44·10	31·20	24·74	10·70	64·56
28·10	23·60	48·30	30·90	1·14	67·96
26·64	36·82	36·54	31·65	0·76	67·59
29·80	26·18	44·02	34·32	0·06	65·62
33·80	10·68	55·52	36·24	—	63·76
36·50	9·17	54·33	39·10	—	60·90
	Solid phase : Tripotassium salt, $6H_2O$.				
37·23	8·65	54·12	39·57	—	60·43
35·77	20·05	44·18	42·14	—	57·86
	Solid phase : Tripotassium salt, $5H_2O$.				
37·03	20·09	42·88	43·62	—	56·38
38·20	20·45	41·35	45·60	—	54·40

Moist solid phase.			Liquid phase.		
K_2O %.	Phenolphthalein anhydride %.	H_2O %.	K_2O %.	Phenolphthalein anhydride %.	H_2O %
Solid phase: Tripotassium salt, $4H_2O$.					
36·51	29·52	33·97	46·49	—	53·51
40·20	19·60	40·20	47·44	—	52·56
Solid phase: Mixture of monopotassium salt and phenolphthalein.					
8·14	51·92	39·94	8·25	25·50	66·25
6·61	58·80	34·59	7·39	23·75	68·86
6·76	64·56	28·68	7·81	24·71	67·48
Solid phase: Mixture of di- and tri-potassium salts.					
19·52	45·97	34·51	17·00	41·00	42·00
17·92	46·33	35·75	16·52	40·80	42·68
Solid phase: Mixture of tripotassium salt and $KOH,2H_2O$.					
38·73	15·91	45·36	45·4	—	54·6

* These experiments were carried out with caustic potash prepared from potassium metal.

UNIVERSITY COLLEGE, READING. [*Received, March 22nd,* 1924.]

CLXXIII.—*Physostigmine (Eserine). Part II. The Synthesis of Physostigmol Ethyl Ether.*

By EDGAR STEDMAN.

BY heating eseroline methiodide at 200° in an atmosphere of carbon dioxide, Straus (*Annalen*, 1913, **401**, 350; 1914, **406**, 332) obtained a crystalline compound, physostigmol, which retained the phenolic hydroxyl group of eseroline and appeared to be an indole compound, since it formed a red picrate and gave the pine-shaving reaction. It contained one *N*-methyl group, and Straus at first considered that its structure was represented by the formula (I)

$$OH\cdot C_6H_3\!<\!\begin{matrix}C(CH{:}CH_2)\\ NMe\text{———}\end{matrix}\!>\!CH,$$

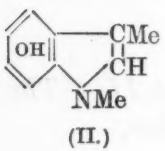
but subsequently abandoned this in favour of (II).

The relationship of physostigmol to eseroline is at present obscure, but it is evident, since the phenolic hydroxyl group which is present in eseroline is retained in physostigmol, that the elucidation of the structure of the latter substance would establish the position of the hydroxyl group relative to the nitrogen atom, which is undoubtedly attached, in eseroline, to the benzene ring.

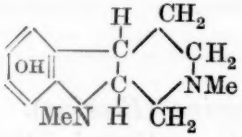
For this purpose, the further degradation of physostigmol (as its ethyl ether) and its synthesis were attempted. When eserethole methiodide was heated under strongly diminished pressure, physostigmol ethyl ether sublimed slowly from the fused mass. Not only

was the ether thus obtained directly, but the method possessed the further advantage that the yield was considerably improved. Numerous unsuccessful attempts were made to degrade physostigmol ethyl ether by oxidation or catalytic reduction; even heating with finely divided nickel at 200° in an atmosphere of hydrogen—treatment by which indole is partly converted into *o*-toluidine (Carrasco and Padoa, *Gazzetta*, 1906, **36**, II, 512), left the ether largely unchanged.

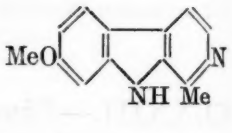
The synthetic method proved successful. Straus has shown that one methyl group in physostigmol is in position 1; that the second is in position 3 was rendered probable by the oxidation experiments mentioned above, for, whereas 2-methylindole is readily converted into acetylanthranilic acid, indole compounds without an alkyl group in position 2 do not undergo smooth oxidation. Despite the resemblance between the formula III, provisionally assigned by Straus to eseroline, and that of harmine (IV; Perkin and Robin-



(II.)

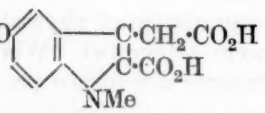


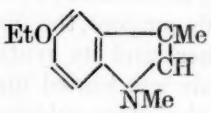
(III.)



(IV.)

son, J., 1919, **115**, 967), experiment indicated that the orientation of the hydroxyl group in the former is not the same as that of the methoxyl in harmine; this result places one more difficulty in the way of the acceptance of Straus's formula for eseroline. It thus seemed most likely that physostigmol is 5-hydroxy-1 : 3 dimethylindole. The synthesis of its ethyl ether was effected by Kermack, Perkin, and Robinson's method (J., 1921, **119**, 1622) for the preparation of certain 3-methylindoles. Methyl-*p*-phenetidine was converted into nitrosomethyl-*p*-phenetidine, which on reduction yielded *p*-ethoxyphenylmethylhydrazine. This condensed with α-ketoglutaric acid to form 5-ethoxy-2-carboxy-1-methylindole-3-acetic acid (V), which, on heating, lost carbon dioxide with the formation of 5-ethoxy-1 : 3-dimethylindole (VI), which is identical with physostigmol ethyl ether. The constitution of this substance is thus established and therewith the position of the hydroxyl group in eseroline.

(V.)




(VI.)

EXPERIMENTAL.

Physostigmol Ethyl Ether.—When eserethole methiodide (0·5 gram) was heated, under the high vacuum of a rotatory oil pump, in a bath at 180°, it melted and a white solid slowly sublimed on to the surface of a cooler placed in the flask; the temperature was finally raised to 220°. The yield of crude material was 0·16 gram (66 per cent.). *Physostigmol ethyl ether* crystallises from ethyl or methyl alcohol in lustrous plates, m. p. 86° (Found: C = 75·67; H = 7·83. $C_{12}H_{15}ON$ requires C = 76·19; H = 7·94 per cent.). With Ehrlich's reagent, it gives a violet coloration, which slowly changes to intense blue.

The *picrate*, prepared from equimolecular quantities of the ether and picric acid in hot alcohol, crystallises from this solvent in dark reddish-brown needles, m. p. 95° (Found: C = 51·4; H = 4·36. $C_{18}H_{18}O_8N_4$ requires C = 51·9; H = 4·3 per cent.).

Nitrosomethyl-p-*phenetidine.*—A mixture of 34 grams of *p*-phenetidine and 39 grams of methyl iodide, after abatement of the initial reaction, was heated under reflux for 2 hours, the viscous product dissolved in water, and the dried ethereal extract of the oil precipitated by sodium hydroxide was distilled after evaporation of the solvent; a colourless oil (30 grams) passed over at 123—126°/12 mm., leaving a small residue of brown tar. This mixture of bases, dissolved in 30 c.c. of concentrated hydrochloric acid and 80 c.c. of water, cooled in a freezing mixture, was slowly treated with 16 grams of sodium nitrite in 100 c.c. of water, and the ethereal extract of the oily nitroso-compound was dried over calcium chloride and evaporated, a dark red oil (24 grams) remaining, which partly crystallised; after 24 hours, the semi-solid mass was drained on porous plate and the crude nitroso-compound obtained as a brick-red solid (yield 8 grams). Recrystallised from alcohol, *nitrosomethyl*-p-*phenetidine* forms buff-coloured plates, m. p. 47—48° (Found: C = 60·0; H = 6·9. $C_9H_{12}O_2N_2$ requires C = 60·0; H = 6·7 per cent.).

as-p-*Ethoxyphenylmethylhydrazine.*—A solution of 6 grams of the crude nitroso-compound in 12 c.c. of glacial acetic acid was slowly added to a cooled, stirred suspension of 25 grams of zinc dust in 45 c.c. of water. After reduction, the mixture was warmed on a steam-bath, the liquid filtered, the residue repeatedly warmed with small portions of dilute acetic acid, and the combined extracts and filtrate were treated with excess of 40 per cent. sodium hydroxide and extracted with ether. The extract was dried over potassium carbonate, filtered, and the ether distilled, leaving 4·2 grams of a slightly brown oil. On distillation, almost pure p-*ethoxyphenyl*-

methylhydrazine, a colourless oil which rapidly darkened, b. p. about 140°/12 mm., was obtained. The *hydrochloride*, prepared by means of concentrated alcoholic hydrogen chloride, crystallised from alcohol in flat prisms, m. p. 129°.

5-*Ethoxy*-2-*carboxy*-1-*methylindole*-3-*acetic Acid* (Formula V).—When the reaction between 2 grams of crude *p*-ethoxyphenylmethylhydrazine and 2 grams of α-ketoglutaric acid in 7 c.c. of warm 50 per cent. acetic acid had subsided, a white solid separating, the mixture was heated in a boiling-water bath for 10 minutes, cooled, and the precipitate of the above indole compound washed with dilute acetic acid and with alcohol (yield 1 gram).

5-*Ethoxy*-2-*carboxy*-1-*methylindole*-3-*acetic acid* crystallised, with slight decomposition, from strong (>50 per cent.) acetic acid in long, narrow prisms, but separated from acetone, in which it was only sparingly soluble, in colourless prisms, m. p. 248° (decomp.; darkening at 220°) (Found: C = 60·4; H = 5·4. $C_{14}H_{15}O_5N$ requires C = 60·6; H = 5·4 per cent.).

5-*Ethoxy*-1 : 3-*dimethylindole* (*Physostigmol Ethyl Ether*) (Formula VI).—The preceding acid was heated at 250° until evolution of carbon dioxide ceased and 5-ethoxy-1 : 3-dimethylindole was distilled from the charred mass under strongly diminished pressure. Recrystallised from methyl alcohol, it formed lustrous plates, m. p. 86°. It was shown to be identical with physostigmol ethyl ether by the colour reaction with Ehrlich's reagent and by the melting point of the mixture. It further formed a picrate identical with that obtained from physostigmol ethyl ether prepared from eserethole methiodide.

In conclusion, the author desires to thank Prof. G. Barger, F.R.S., for his suggestions in connexion with this work.

The expense of the material employed in the synthesis was met by a grant from the Earl of Moray Research Fund of this University, whilst the physostigmine was purchased with a grant made to Prof. Barger by the Administrators of the Carnegie Trust for the Scottish Universities; this assistance is gratefully acknowledged.

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CLXXIV.—*The Orienting Influence of the Thiocyano-group in Aromatic Compounds.*

By FREDERICK CHALLENGER and ALFRED DREW COLLINS.

IT has been shown by Söderbäck (*Annalen*, 1919, **419**, 217) and by one of the authors that, in its behaviour towards organic compounds thiocyanogen resembles the halogens, and particularly iodine. This conclusion is confirmed by the work of Kaufmann and Liepe (*Ber. deut. Pharm. Ges.*, 1923, **33**, 139; *Ber.*, 1923, **56**, [*B*], 2514) and by the unpublished observations of Challenger and Bott on its behaviour towards methyl styryl ketone and dibenzalacetone.

It was therefore of interest to study the properties of the thiocyano-group when present in the benzene nucleus. That a general resemblance to the halogens in chemical properties does not necessarily involve similar orientation follows from the meta-substitution induced by the cyanogen radical in benzonitrile. This is, however, readily explicable on the principle of induced alternate polarities.

From the same theory, it appeared probable that the thiocyano-group would possess ortho-para-directing influence. Apart from the (not oriented) nitration of *m*-dithiocyanobenzene (Gabriel, *Ber.*, 1877, **10**, 184), the direct introduction of nitro- or other groups into aromatic thiocyanates has not been described.

The present communication contains an account of the nitration of phenyl thiocyanate, its *p*-chloro-, *p*-bromo-, and *p*-iodo-derivatives, and of *p*-tolyl thiocyanate. Ordinary nitric and sulphuric acids at 5—10° were employed in all cases. The constitution of the products of nitration has been determined by comparison with nitro-thiocyanates of known structure, or by conversion into disulphides. *o*-Nitrophenyl thiocyanate was identified by reduction to 1-aminobenzothiazole.

The results are presented in tabular form; in the case of isomerides, that produced in minor amount is indicated by a bracketed figure. The positions of SCN and R in $R{\cdot}C_6H_4{\cdot}SCN$ are 1 and 4, respectively.

Expt.	A	B	C	D	E
R	H	Cl	Br	I	Me
NO_2 enters position	4(2)	2	2	4	3(2)

The elimination of iodine in D is analogous to that observed by Holleman (*Rec. trav. chim.*, 1915, **34**, 222) on nitration of *p*-chloro- and *p*-bromo-iodobenzene (compare also *Ber.*, 1897, **30**, 3000; 1898, **31**, 1710). In the first case, *p*-chloronitrobenzene was formed,

whilst on nitration of *p*-bromoiodobenzene we have isolated *p*-bromonitrobenzene.

Holleman ("Die Direkte Einführung von Substituenten in den Benzolkern," 1910, 466) concludes that the order

$$OH > NH_2 > Cl > I > Br > Me$$

represents the relative velocities with which these groups induce substitution in the nucleus, but that iodine, bromine, and methyl differ only slightly from each other and that the order is somewhat uncertain. Further work will be necessary to determine with certainty the relative speeds of substitution induced by Me, SCN, and the halogens. The predominating, if not exclusive, production of the 2-nitro-derivatives in B and C shows, however, that, as regards the velocity with which it induces substitution, the –SCN group is more powerful than chlorine or bromine.* Experiment E would indicate that methyl is more powerful than thiocyanogen. On nitration of toluene, about 56 per cent. of the ortho-compound is obtained, whilst phenyl thiocyanate gives relatively little *o*-nitro-derivative.

Experimental.

Nitration of Phenyl Thiocyanate.—Ten grams of the thiocyanate were nitrated at 5—10° in the usual way with 34 grams of nitric acid (*d* 1·41) and 50 grams of sulphuric acid, a yellow solid forming, and the mixture was poured on ice. The solid (m. p. 110°; 12·5 grams; 94 per cent. yield) was crystallised from alcohol, when *p*-nitrophenyl thiocyanate (Müller, *Z. farb. Text. Ind.*, 1906, **5**, 357), m. p. 133°, was isolated. This depressed the m. p. of *o*-nitrophenyl thiocyanate (132·5°) to 112—114°, and that of 2 : 4-dinitrophenyl thiocyanate (139°) to 120°. It was converted by boiling alcoholic ammonium sulphide into 4 : 4′-dinitrodiphenyl disulphide, m. p. 181° (the *o*-compound has m. p. 193°). On further nitration with two parts of nitric acid (*d* 1·41) and three parts of sulphuric acid at about 90°, it yielded 2 : 4-dinitrophenyl thiocyanate, m. p. and mixed m. p. 138—139°.

The soluble fractions, m. p. about 100°, obtained on crystallisation of the crude mononitrophenyl thiocyanate were reduced with stannous chloride in hydrochloric acid, the tin was removed, and the concentrated solution treated with lead acetate. The solution of the yellow mercaptide in dilute acid was freed from lead, treated with ammonia, and oxidised by air, giving 4 : 4′-diaminodiphenyl disulphide. The filtrate from the mercaptide was treated with

* As a result of later work, Holleman finds $OH > NH_2 > I > Cl > Br$ (*Rec. trav. chim.*, 1915, **34**, 204), from which the similarity between iodine and thiocyanogen is again apparent.

sodium hydroxide and the precipitate extracted with hot water. The solution deposited 1-aminobenzothiazole, m. p. and mixed m. p. 128—130° (Müller, *loc. cit.*).

Nitration of p-*Tolyl Thiocyanate.*—Thiocyanate 11 grams, nitric acid 40 c.c., sulphuric acid 40 c.c. After 3 hours at 20°, the mixture was poured on ice. The precipitate (m. p. below 60°) was dissolved in its own bulk of hot alcohol, which on cooling deposited 3-nitro-*p*-tolyl thiocyanate, m. p. 125° on recrystallisation (Found : N = 14·24. Calc., N = 14·43 per cent.). The main product of nitration, 2-*nitro*-p-*tolyl thiocyanate*, was isolated from the alcoholic mother-liquors. It was also prepared from diazotised 2-nitro-*p*-toluidine by the following method; faintly yellow needles, m. p. 40° (Found : N = 14·25. $C_8H_6O_2N_2S$ requires N = 14·43 per cent.).

3-*Nitro*-p-*tolyl Thiocyanate.*—Twelve grams of 3-nitro-*p*-toluidine in 120 c.c. of sulphuric acid (1 : 5) were diazotised at 6° and slowly added to 21·5 grams of cuprous thiocyanate and 10 grams of the potassium salt in cold water. The product was extracted with hot alcohol, giving yellow leaflets, m. p. 125°, in excellent yield (compare Zincke and Röse, *Annalen*, 1914, **406**, 103) (Found : N = 14·04. Calc., N = 14·43 per cent.).

p-*Bromophenyl thiocyanate* was similarly prepared from diazotised *p*-bromoaniline and distilled in steam; m. p. 56° on crystallisation from alcohol (Found : N = 6·38; Br = 37·35. C_7H_4NBrS requires N = 6·54; Br = 37·39 per cent.). The non-volatile solid, on extraction with alcohol, gave 4 : 4′-dibromodiphenyl disulphide, m. p. 92—93°.

p-Bromophenyl mercaptan, m. p. 74°, was obtained on boiling the thiocyanate with alcoholic potassium hydrosulphide and acidifying. With alcoholic ammonia in air, it gave the disulphide, m. p. 93—94°. Hübner and Alsberg give m. p. 75° and 93·5°, respectively (*Annalen*, 1870, **156**, 328).

Nitration of p-*Bromophenyl Thiocyanate.*—Thiocyanate 3·5 grams, nitric acid 10 c.c., sulphuric acid 10 c.c. The yellow solid, sintering from 50—115°, crystallised from alcohol in long, yellow needles (Found : N = 11·08 per cent.) of constant m. p. 131°, not depressing the m. p. (131°) of 4-*bromo*-2-*nitrophenyl thiocyanate* prepared from diazotised 4-bromo-2-nitroaniline (Found : Br = 30·35, 30·91. $C_7H_3O_2N_2BrS$ requires N = 10·81; Br = 30·89 per cent.). Potassium hydrosulphide converted it into potassium thiocyanate and 4-bromo-2-nitrophenyl mercaptan, m. p. 110°, which was oxidised to 4 : 4′-dibromo-2 : 2′-dinitrodiphenyl disulphide, m. p. 174° (Blanksma, *Rec. trav. chim.*, 1901, **20**, 121, 399).

The alcoholic mother-liquors from the crude nitration product yielded traces of a solid bromo-thiocyanate, m. p. about 95°. This

may have contained the 3-nitro-derivative, but even from a further nitration using 13 grams of *p*-bromophenyl thiocyanate only the 2-nitro-derivative could be obtained in a pure condition, the quantities of the other products being too small for investigation.

p-*Chlorophenyl Thiocyanate and its Nitration.*—The thiocyanate (see Hantzsch and Hirsch, *Ber.*, 1896, **29**, 947) was prepared from diazotised *p*-chloroaniline; 4 : 4′-dichlorodiphenyl disulphide, m. p. 70—71°, was also produced.

Nitration :—Thiocyanate 4 grams, nitric acid 14·5 c.c., sulphuric acid 18·5 c.c. The product melted at 116·5° after crystallisation from alcohol and did not depress the m. p. of 4-chloro-2-nitrophenyl thiocyanate (Zincke and Baeumer, *Annalen*, 1918, **416**, 86). It was converted into the corresponding disulphide, m. p. 212° (Blanksma, *loc. cit.*). No trace of an isomeric thiocyanate could be found.

p-*Iodophenyl Thiocyanate.*—This substance, which could not be prepared from diazotised *p*-iodoaniline, the di-iodo-disulphide being always produced, was obtained from crude thiocyanoaniline (Söderbäck, *loc. cit.*, p. 271), which was converted into the hydrochloride, diazotised, and treated with potassium iodide. The oil obtained on steam distillation was crystallised from dilute alcohol; m. p. 51—52°. It reacted with potassium hydrosulphide to yield a mercaptan, which was oxidised to 4 : 4′-di-iododiphenyl disulphide, m. p. and mixed m. p. 124° (Baumann and Schmitz, *Z. physiol. Chem.*, 1895, **20**, 593).

Nitration of p-*Iodophenyl Thiocyanate.*—Thiocyanate 4 grams, sulphuric acid 13 c.c., nitric acid 12 c.c. The yellow solution soon deposited a dark solid, and after 3 minutes was poured on ice. The precipitate was freed from much iodine with potassium iodide and fractionally crystallised, yielding a small amount of a halogen-free substance, m. p. 129—131°, which did not depress the m. p. of *p*-nitrophenyl thiocyanate.

2 : 4-*Dinitrophenyl Thiocyanate and Selenocyanate.*—When 1 : 2 : 4-trinitrobenzene was boiled with alcoholic potassium thiocyanate (or selenocyanate), the 2 : 4-dinitro-derivative of phenyl thiocyanate (or selenocyanate *) was obtained (m. p. and mixed m. p.).

In the preparation of 2 : 4-dinitrophenyl thiocyanate from 2 : 4-dinitrochlorobenzene (compare Austen and Smith, *Amer. Chem. J.*, 1886, **8**, 90; Hinsberg, *Ber.*, 1906, **39**, 4331), we have noticed the formation of 2 : 4 : 2′ : 4′-tetranitrodiphenyl sulphide, m. p. 195°, and also of the corresponding disulphide. Successive extraction with alcohol, acetone, and chlorobenzene separates the three ingredients.

* From the nitration product of phenyl selenocyanate, which does not appear to have been described, the *p*-nitro-derivative may be isolated,

Mobility of the Thiocyano-group in 2 : 4-Dinitrophenyl Thiocyanate.—When the thiocyanate was warmed with aniline a red addition product, stable to light petroleum, was produced. This was decomposed by cold methyl alcohol, regenerating the thiocyanate.

When the dinitro-thiocyanate was boiled for some hours with alcoholic aniline, a red solid formed which, on crystallisation from alcohol, gave much 2 : 4-dinitrodiphenylamine, m. p. and mixed m. p. 153°, and also yellow needles, m. p. 192°, which did not depress the m. p. of 2 : 4 : 2′ : 4′-tetranitrodiphenyl sulphide. A trace of insoluble residue, m. p. above 280°, closely resembled the corresponding disulphide.

The alcoholic mother-liquors yielded a solid, m. p. 151—152°, which, with mercuric oxide in boiling toluene, gave mercury sulphide, whilst, with acetic anhydride, the odour of a mustard oil was produced. The substance depressed the m. p. of thiocarbanilide, but not of phenylthiocarbamide, which was obtained by Schiff (*Annalen*, 1868, **148**, 338) from aniline and ammonium thiocyanate. The compound was produced from aniline and the thiocyanic acid eliminated during the reaction; we have also prepared it from aniline and an ethereal solution of thiocyanic acid. *p*-Toluidine similarly gives *p*-tolylthiocarbamide, m. p. 188°.

Aniline and o-*Nitrophenyl Thiocyanate.*—Equal weights were boiled for 2½ hours. Extraction with hot alcohol left di-*o*-nitrophenyl disulphide, m. p. 193° (Found: N = 9·08. Calc., N = 9·09 per cent.). The alcoholic extract yielded volatile, yellow needles with the m. p. (122—123°) of di-*o*-nitrophenyl sulphide. No derivative of diphenylamine was isolated.

The authors desire to express their thanks to the Research Fund Committee of the Chemical Society for a grant in aid of this investigation.

THE UNIVERSITY, MANCHESTER. [*Received, March 28th*, 1924.]

CLXXV.—*Induced Alternate Polarities in a Carbon Chain on the Basis of Bohr's Theory.*

By KRISTIAN HØJENDAHL.

THE object of this paper is to investigate the problem of induced polarity from the point of view of the Rutherford-Bohr atom-model in the form given recently by Bohr (compare *Nature*, 1923, **112**, 29).

According to this, the valency electrons describe rosettes round the nucleus. The reason why rosettes appear instead of ellipses is that the force field is stronger inside the inner electron shells. In passing from lithium to carbon, the difference between the inside and the outside of the shells will diminish and therefore it can be understood why the rotation of the ellipse can be overcome in the case of carbon atoms chemically bound, whilst this cannot be the case for lithium.*

The problem of the formation of non-polar organic compounds on the basis of the Bohr concepts has only recently been attacked. From a mechanical point of view, the question in its simplest form is: What is the nature of the path followed by a particle when moving symmetrically around two centres of attraction? A configuration representing the two nuclei as situated at the foci of the elliptic orbit described around them has been examined by Marshall (*Proc. Roy. Soc. Edin.*, 1922, **42**, 247) and similar cases by Pauli (*Ann. Physik*, 1922, **68**, 177). It is probable, however, that the normal orbit of each electron as suggested by Sidgwick is more correctly represented (because more stable) by an alternative configuration, namely, a figure-of-eight with a nucleus at the centre of each of the two loops. Each of the two electrons (which together constitute the single bond) follows a double-looped path, the plane of the path of one electron being perpendicular to the plane of the other. This model and some of the conditions which it must fulfil have been discussed by Fowler and Sidgwick (*Trans. Faraday Soc.*, 1923, **19**, 459, 469). They draw the following conclusions.

The orbits (of the two electrons constituting the covalent bond) represent or replace a 2_1 and a 2_2 orbit in each atom.

All the electrons shared (or unshared) by any one atom have to pass through their perinuclear in due succession, hence their periods must agree; moreover, in a chain of atoms the periods of all the binuclear orbits must be the same or differ rationally. This may be termed conveniently the "frequency-condition."

The laws of symmetry and stability which characterise the orbits of electrons in free atoms, and particularly completed groups of orbits, apply to a considerable extent even to the outer orbits of the atom when in combination. This may be termed the "symmetry-condition."

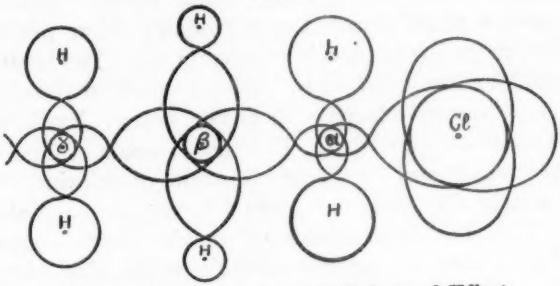
The first conclusion means that when all the four valencies of a carbon atom have been bound in a compound, the atom contains four 2_1 and four 2_2 orbits and therefore forms a neon structure.

* The author hopes to show elsewhere how the rosette in the case of lithium leads to the known properties of a metallic substance.

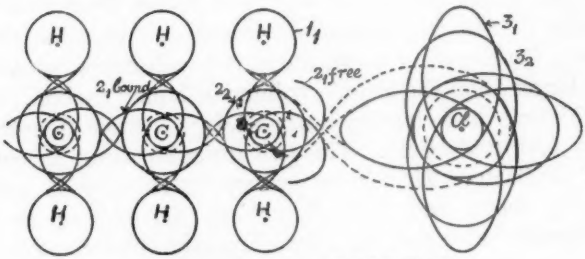
It is most probable that each electron in the bond describes a 2_1 orbit round one nucleus and a 2_2 orbit round the other; but this is not necessary for the treatment which follows.

The Concept of Alternate Induced Polarities on the above Basis.—This concept (which also embodies the α–γ rule) has been intro-

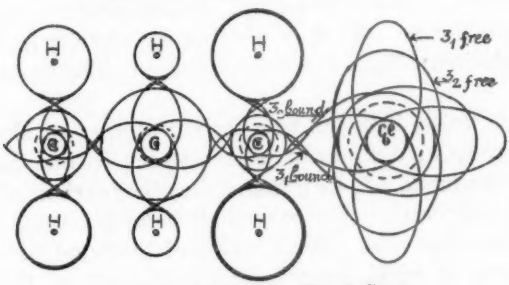
FIG. 1.



Skeleton Diagram. General Nature of Effect.



Complete Diagram. Initial State.



Complete Diagram. Final State.

duced by Lapworth, and Kermack and Robinson (J., 1922, **121**, 416, 427). It states that if an electronegative atom is introduced into a carbon chain, the α-carbon atom, to which it is bound, becomes "positive," the β-atom "negative," the γ-atom "positive," and so on.

To show how this may be deduced on the basis of the present

bond-theory, the case of chlorine bound to a long paraffin chain is considered. For convenience, all the orbits are represented in the plane of the paper. In reality, the orbits are arranged in space and they are probably not even plane themselves. Symmetry in space is represented by symmetry in the plane. The first diagram in Fig. 1 shows a simplified case, where the two loops of the electron orbits are assumed to be equal. The other two diagrams give a more detailed and probably truer picture of the molecule before and after the binding process. The treatment has been confined to the latter case. With respect to the dimensions, these are not known exactly; it is the energy levels which are known with greater precision. For the 1_1 orbit of hydrogen, the 2_1 orbits of carbon, and the 3_1 and 3_2 orbits of chlorine, the energy levels are nearly the same (compare Supplement to *Nature*, 1924, **113**, 218, Fig. 1). [The statement made above suggests that covalent bonds are in general possible when the energy levels (*i.e.* the frequencies) of the electrons of the combining atoms are approximately the same.] It seems to follow from this that the dimensions of the *free* atoms of carbon and chlorine are nearly the same. On the other hand, the atomic volume of bound chlorine is much larger than the atomic volume of bound carbon.

The chlorine atom has an inner electron system denoted in the figure by a dotted circle. The two inner electrons in carbon are denoted similarly. This inner system in chlorine is surrounded by four 3_1 orbits and three 3_2 orbits. By sharing an electron orbit originally belonging to carbon alone, the chlorine atom becomes an *argon* structure. The shared orbit is taken up as a fourth 3_2 orbit. To form a *neon* structure, carbon needs a 2_2 orbit from the side of chlorine. This it obtains by sharing one of the 3_1 orbits of chlorine. Thus the bond between chlorine and carbon is formed.

As regards union between two carbon atoms, an electron which originally occupied a 2_1 orbit with respect to one carbon atom, commences to pursue a 2_2 loop round the other carbon atom, thereby providing a half bond. The other half bond is formed in the same way from the other side. For the case of the bond between carbon and hydrogen, it must be assumed that each of the two loops round the hydrogen nucleus represents a 1_1 orbit.

The two conditions referred to above, namely, the "frequency-condition" due to Sidgwick and the "symmetry-condition" due to Fowler, may now be applied to the different atoms in the molecule.

First it will be realised that the dimensions of bound carbon will be considerably smaller than those of a free carbon atom, because in the former the valency electron has to pass through a

2_1 and a 2_2 loop in the same time as is required for passing round in a 2_1 orbit in free carbon.

This is not the case for the chlorine atom. Here the frequency condition requires that the frequency (*i.e.* the reciprocal of the time occupied for a full revolution) in a shared 3_1 orbit is exactly the same as that for a full revolution in an unshared 3_1 orbit. The symmetry condition, on the other hand, requires that the 3_1 loop of a shared orbit shall be as similar as possible to an unshared 3_1 orbit. Both these conditions cannot be fulfilled. As the "frequency-condition" is absolute, it is the "symmetry-condition" which gives way to a certain extent. Nevertheless, the "symmetry-condition" requires that the loop of the shared electron round chlorine shall become as large as possible, with the result that the loop round the α-carbon atom decreases below its normal size in order to maintain constancy of the total time taken to complete a revolution. In other words, the chlorine atom is not as flexible as the carbon atom and the atomic volume of chlorine is not very different in the bound and in the free state, respectively. This provides a reason for the fact that although the dimensions of the free atoms decrease all the way through a period in the periodic system, the atomic volumes of bound atoms, on the other hand, increase towards the end of a period.

The uniqueness of carbon as a bond-forming atom probably depends on its flexibility.

Also as regards the other half of the bond, the 3_2 loop round chlorine will persist in magnitude and the 2_1 loop round the α-carbon atom will be smaller than normal for the same reason as before.

Applying the "symmetry-condition" to the α-carbon atom, it will be seen that all the loops round this atom will decrease in size as compared with their normal magnitude. As the effective velocity of an electron is increased by decreasing the dimensions of the path, it will be realised that *the time during which the carbon atom has electrons in its neighbourhood is shortened*, with the result that the α-carbon atom becomes positively charged relative to contiguous atoms.

It is in this sense, and in this sense only, that the terms positive and negative can be legitimately applied in the system under consideration.

Considering the bond between the α- and the β-carbon atom, the "frequency-condition" requires that the time for a full revolution is kept constant. The time intervals in which the valency electrons are associated with the α-carbon atom are shortened, as we have seen, and therefore the time during which they revolve in the neighbourhood of the β-carbon atom must be prolonged.

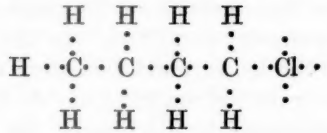
Due to the "symmetry-condition," all the valency electrons associated with an atom will tend to behave similarly, with the result that the β-atom becomes negatively charged. Proceeding in this manner, it will be seen that the γ-atom becomes positively charged and the δ-atom negatively charged, and so on.

This is identical with the general statement of alternating polarities.

As is evident from the figure, the mode of picturing structures and bonds is not convenient for general use. For the purpose of formal representation on the basis of the above considerations, it is therefore of interest to see how a Bohr structure can be harmonised with the schematic system of G. N. Lewis, where electrons are represented by fixed points. The frequency condition may be expressed by constant distances between the atoms and the symmetry-condition by a symmetrical arrangement of the electrons round the atom. The representative point may be taken as the mean or average position of the electron during a complete revolution. Hence a single bond will be represented thus

C· ·C instead of C:C.

The formal change here considered might be regarded as trifling. It represents, however, in the author's opinion, a distinct advance in that it indicates a structure more nearly approximating to physical reality. The double bond accordingly would be C: :C. The molecule already considered by way of illustration would therefore be represented by

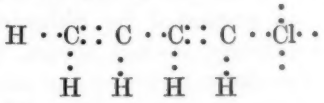


We now turn to the question of the persistence of alternation of polarities as we pass from the key atom. The effect decreases, as is verified by experiment, as we pass farther from the electronegative atom; but the decrement has a different magnitude according to the nature of the chain. As all electron orbits with the same quantum-numbers are symmetrical and the deformation of the orbits also is symmetrical, it is reasonable to assume that equal stresses are set up in them. The total stress arising in this way in the atom balances the stress from the orbits which cause the deformation.

For the case of the paraffin chain this means that the stress from the chlorine atom on the α-carbon atom is distributed equally on the three other atoms bound to the α-carbon atom. Hence

one-third of the original stress is carried over to the β-atom, one-ninth to the γ, and so on. The actual effects on the carbon atoms may therefore be represented by the progression $+1 - 1/3 + 1/9 - 1/27 + 1/81$, the signs indicating that the stresses on contiguous atoms oppose one another. As will be seen, the effect decreases to negligible dimensions relatively rapidly.

In the case of alternating single and double bonds

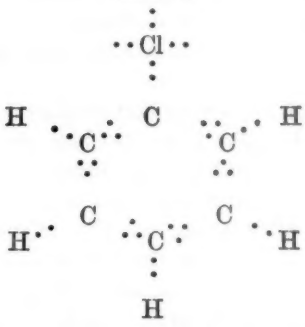


the stresses diminish according to the progression $+1 - 2/3 + 1/3 - 2/9 + 1/9$.

In agreement with experiments, the decrease is much slower than in the paraffin chain.

The principle of alternation has long been recognised in aromatic compounds in the similarity between ortho- and para-isomerides. According to Robinson (*loc. cit.*) and others, it is assumed that the benzene ring contains three electronic bonds as shown in Fig. 2.

FIG. 2.



The stress in this case divides itself into two parts, which travel round the two sides of the ring, forming, in fact, alternate large and small loops around successive nuclei. With respect to one portion of the stress this diminishes according to the progression

$$+1 - 1/2 + 3/10 - 9/50 + 27/250 - 81/1250$$
$$\text{ortho} \quad \text{meta} \quad \text{para} \quad \text{meta} \quad \text{ortho}$$

The total stress is obtained by adding the two portions together. Thus we obtain, for ortho $-1/2 - 81/1250 = -0{\cdot}565$, for meta $+3/10 + 27/250 = +0{\cdot}408$, and for para $-9/50 - 9/50 = -0{\cdot}360$.

It will be observed that ortho and para have the same sign and that the effect is strong all the way round the ring.

Summary.

(1) Using the concepts of Bohr, the attempt is made to find a physical basis for the existence of alternate polarities in a substituted carbon chain.

(2) In agreement with the accepted view, the non-polar, covalent bond is regarded as consisting of two electrons revolving in orbits which are perpendicular to one another, each orbit having the shape of a figure-of-eight, as suggested by Sidgwick. In an isolated diatomic molecule consisting of like atoms, the two orbits are identical in size and the electrons are in the neighbourhood of each nucleus during the same time intervals. When the atoms are unlike, these two time intervals are no longer the same, because the loops are unequal in size.

(3) It is assumed that two fundamental principles are valid, namely, the "frequency-condition" of Sidgwick and the "symmetry-condition" of Fowler.

(4) On the basis of these considerations, it is shown that the terms positive and negative as conventionally employed to represent a property of different atoms in an organic molecule correspond physically to small and large loops, respectively, in any completed orbit. In this sense, therefore, a negative atom is one in which the valency electrons remain for a relatively long time interval in the neighbourhood of the nucleus.

(5) The resistance of positivity and negativity (as defined above) as a function of the distance from the key atom is considered and a semiquantitative treatment of the decrement carried out.

(6) The case of the benzene molecule is considered. It is shown that numerically the alternating polarity effect persists round the entire ring. Numerical values of the extent and sign of the polarity are attributed to the ortho-, meta-, and para-positions, respectively.

(7) As the diagrammatic representation of the orbits physically involved leads to complicated structures, a slight modification of the conventional representation of the G. N. Lewis configuration is suggested to represent the application of the Bohr concepts to covalent bonds.

The author desires to express his thanks to the Ramsay Memorial Fellowship Trust for a grant which enabled the above work to be carried out.

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CLXXVI.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XXII. Some Compounds containing the Secondary Octyl Radical Linked to Oxygen.*

By HAROLD HUNTER.

WHATEVER may be the significance ultimately attached to natural rotatory dispersion, it is now an established experimental fact that optically active organic compounds may be divided into two classes: those of which the rotatory dispersion in the limited range of the spectrum available to measurement may be expressed by one term of Drude's dispersion equation, $\alpha = \Sigma k_n/(\lambda^2 - \lambda_n{}^2)$; and those which require more than one such term. The latter type of dispersion—"complex," as it is usually termed—has hitherto been associated almost entirely with acids and esters; the carboxyl group or one of its equivalents, the carboalkyloxyl group or the xanthogenic ester group, nearly always appears in the formula of a compound which exhibits complex rotatory dispersion. The simpler alcohols, on the other hand, so far as available measurements go, rarely require more than a one-term Drude equation: the rotatory dispersions of these are said to be "simple."

In view of the considerations brought forward in Part XXI (this vol., p. 1198), it seems undesirable to insist on a distinction between simple and complex rotatory dispersion as far as theories are concerned, and therefore it is proposed, in this paper at least, to restrict the discussion to a classification of the observed facts of rotatory dispersion. The following table contains those so far observed: R represents the β-octyl group, and R′ a *n*-alkyl group.

Compounds of which the observed rotatory dispersion is:

Apparently Simple.	*Obviously* Complex.
R·OH secondary alcohol.	R′·C(=O)·OR carboxylic ester
R·O·R′ ethers.	
$CH_2(OR)_2$ formal.	
$CH(OR)_3$ orthoformate.	
RO·CO·OR symmetrical carbonate.	R·O·N:O nitrite.*
RO·CO·OR′ unsymmetrical carbonate.	
RO·SO·OR sulphite.	

* The author is indebted to Prof. H. E. Merwin, of the Geophysical Laboratory, Washington, D.C., U.S.A., for pointing out an arithmetical mistake in Part XIX (J., 1923, **123**, 434), where the refractive index of *d*-γ-nonyl nitrite is given as 1·4384 for $\lambda = 4358$. This figure should read $n_{4358}^{20°} = 1{\cdot}4284$. The refractive dispersion of this compound now shows a proper relation to those of *iso*butyl and *iso*amyl nitrites as observed by Brühl.

It must be clearly understood that this classification is provisional only, and may be considerably modified if measurements in other parts of the spectrum become available. It has already broken down in some cases; thus there are some secondary alcohols which show complex rotatory dispersion. These, however, generally contain an aromatic nucleus, at present an unknown factor as far as rotatory dispersion is concerned. Further, in the next paper there is described a series of ethers exhibiting complex rotatory dispersion, whilst, on the other hand, there are two series of esters (see Parts XI and XVIII, J., 1915, **107**, 35; 1923, **123**, 105), both apparently exhibiting simple rotatory dispersion. Broadly, however, this classification represents the behaviour of β-octyl compounds when observations are confined to the visible, and in some cases even when they are extended to the near ultra-violet, region of the spectrum. In view of the considerations discussed in Part XXI (*loc. cit.*), however, it would be rash to ignore the possibility that observations pushed farther into the ultra-violet, that is to say nearer to the absorption band or bands dominating the rotatory dispersion of the compound under consideration, may modify this provisional classification.

As far as these observations go, however, it may be said that the complex rotatory dispersion associated with the carboxyl group or its equivalents is due to the presence, in one molecule, of both a singly and a doubly linked oxygen atom, arranged unsymmetrically. It will be seen that β-octyl compounds containing only saturated oxygen atoms, such as the alcohol, the formal, the orthoformate, and the ethers, exhibit rotatory dispersions which are apparently simple, whilst those containing a doubly bound oxygen atom—the esters—show rotatory dispersions which are obviously complex. The exceptions to this statement are the carbonates and the sulphite. In these cases, it is suggested that the saturated oxygen atoms are distributed symmetrically about the unsaturated one, and that this arrangement is sufficient to suppress any obvious complexity of rotatory dispersion.

Some of the experimental figures are noteworthy. Di-*d*-β-octylformal has a very high rotatory power which decreases rapidly with rise of temperature. This compound shows apparently simple

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Furthermore, the Sellmeier equation for this compound now contains two terms, thus:

$$n^2 = 2{\cdot}0266 + \frac{0{\cdot}00127}{\lambda^2 - 0{\cdot}14} - 0{\cdot}0626\ \lambda^2$$

and is at once comparable with the Drude equation for the same substance. With the above equation, the observed and calculated values for its refractive index agree within ± 0·0001 for each wave-length employed.

rotatory dispersion and yet possesses a rotatory power which is exceedingly sensitive to change in external conditions, a sensitivity which has been associated since the time of Biot with anomalous, and hence complex, dispersion. The Drude equation for the formal at 20° is quoted in the experimental part. On account of the difficulty of obtaining measurements of sufficient precision at higher temperatures no attempt has been made to fit Drude equations to these figures, but the dispersion remains apparently simple throughout the experimental range of temperature, and, as indicated by the constancy of the dispersion ratio ($\alpha_{4358}/\alpha_{5461}$), the dispersion constant, λ_0^2, is apparently independent of temperature. Tri-*l*-β-octyl orthoformate, although similar in constitution to the formal in that it is the next higher homologue, containing one more optically active β-octyloxyl group, yet exhibits a lower rotatory power, both specific and molecular, than the formal. This is entirely different from the case of ethyl *d*-β-octyl and di-*d*-β-octyl carbonates, of which the latter has a specific rotatory power practically double that of the former. Finally, it should be noted that the rotatory power of di-*d*-β-octyl sulphite is negative, its optical behaviour in this respect being analogous to that of the lævorotatory *d*-β-octyl formate (Part XIII, J., 1923, **123**, 1).

Experimental.

All the compounds described herein were prepared from optically pure β-octanol, $[\alpha]_{5461}^{16°} \pm 11{\cdot}72°$, and were distilled under diminished pressure until the refractive index and rotatory power were constant.

Di-d-β-*octylformal*, $CH_2(O{\cdot}C_8H_{17})_2$, was prepared by Trillat and Gambier's method (*Bull. Soc. chim.*, 1889, [iii], **2**, 817) by heating together at 100° for 4 hours, β-octanol (12 grams), trioxymethylene (5 grams), and anhydrous ferric chloride (0·4 gram). After the action, the mixture was diluted with ether, washed repeatedly with water, dried over anhydrous potassium carbonate, and distilled, a clear, colourless, mobile liquid with a faint, fragrant odour, b. p. 175—177°/16 mm., being obtained.

d-β-*Octyl chlorocarbonate*, $C_8H_{17}{\cdot}O{\cdot}COCl$, prepared by dropping slowly a solution of 100 grams of carbonyl chloride in a litre of toluene into a solution of 149 grams of *d*-β-octanol in 90 grams of pyridine, cooled in a mixture of ice and salt, had the following physical constants: b. p. 92°/13 mm., $d_{4°}^{19°}$ 0·9748, $n_D^{20°}$ 1·4282, $\alpha_{100\text{ mm.}}^{19°}$ λ 5893, + 23·78°; λ 5780, + 24·78°; λ 5461, + 28·06°; λ 4358, + 46·33°; whence $\alpha_{4358}/\alpha_{5461} = 1{\cdot}651$.

Ethyl d-β-*Octyl Carbonate*, $EtO{\cdot}CO{\cdot}O{\cdot}C_8H_{17}$.—*d*-β-Octyl chlorocarbonate (8·8 grams) was slowly dropped into a well-cooled solution of ethyl alcohol (2·3 grams) in 30 grams of pyridine. The mixture

was washed, dried, and distilled in the usual way. A second preparation from ethyl chlorocarbonate and *d*-β-octanol had exactly the same rotatory power. The ester is a fragrant, limpid liquid, b. p. 110°/14 mm.

Di-d-β-*octyl carbonate*, $(C_8H_{17}\cdot O)_2CO$, b. p. 168°/13 mm., was prepared from *d*-β-octanol and *d*-β-octyl chlorocarbonate exactly as before.

Tri-l-β-*octyl Orthoformate*, $(C_8H_{17}\cdot O)_3CH$.—Five grams of ethyl orthoformate were heated for 30 hours at 140° ± 5° with 15 grams of *l*-β-octanol, a volatile liquid (mainly ethyl alcohol) distilling in considerable quantity at first. The fraction, b. p. 195—205°/*ca.* 1 mm., was redistilled. Some decomposition was noticed during the distillation and the rotatory power (α_{5461} 25 mm.) varied from − 6·25° to − 6·20°. The orthoformate is a nearly odourless liquid, b. p. 202—203°/*ca.* 1 mm., $d_4^{15°}$ 0·8592, $n_D^{15°}$ 1·4376, whence $[R_L]^{15°}_{5896} = 122{\cdot}38$ [Calc. for $(C_8H_{17}\cdot O)_3CH$, 122·58; the corresponding figures for $(C_8H_{17}\cdot O)_2CH\cdot OEt$ are, calc. 94·87, obs. 96·52].

Di-d-β-*octyl Sulphite*, $(C_8H_{17}\cdot O)_2SO$.—To 26 grams of *d*-β-octanol in 200 c.c. of dry light petroleum a solution of thionyl chloride (12 grams) in 200 c.c. of the same solvent was added very slowly at − 10° to − 5° with vigorous shaking. Much hydrogen chloride and very little sulphur dioxide were evolved. After 12 hours, the petroleum was removed on the water-bath and the ester distilled. It is a mobile, practically colourless and odourless liquid, b. p. 133—134°/1 mm. After hydrolysis for 1 hour with alcoholic caustic soda, the sulphite was estimated by means of iodine absorption in acid solution [Found : S = 10·61. $(C_8H_{17}\cdot O)_2SO$ requires S = 10·46 per cent.].

Physical Measurements.

Densities were determined in a pyknometer holding about 1·5 c.c., and are referred to water at 4°.

Refractive indices were determined in a jacketed Pulfrich refractometer with water circulation from a thermostat. The sodium and lithium flames, the enclosed mercury and cadmium arcs, the open copper arc, and the neon * lamp were used as light sources. For use with the copper and neon lines the refractometer prism was calibrated with quartz.

Polarimetric measurements were made visually and photographically, the sodium and lithium flames, the enclosed mercury

* The author is indebted to the Director of the Research Laboratories of the General Electric Co., Wembley, for the loan of a new type of neon glow lamp working on 220 volts D.C. This lamp is exceedingly convenient for refractometric work, as the glow is concentrated on a very small cathode.

and cadmium arcs, and the open iron arc being used as light sources. Jacketed tubes were employed with water circulation for the photographic and visual readings at 20°, and hot-oil circulation for the visual readings at higher temperatures. All values were observed in a 50 mm. tube.

Di-d-*β*-*octylformal*.

$t°$.	17·0	46·5	75·5	97·5	128·0	157·5
d.	0·8523	0·8307	0·8071	0·7883	0·7658	0·7427

λ	6438	5896	5461	5086	4800	4678	4358
$n_{\lambda}^{20·6°}$	1·4295	1·4314	1·4334	1·4352	1·4371	1·4379	1·4409

Rotatory power.

α_{6438} + 12·89° at 13·5°; 12·35° at 17·5°; 11·13° at 30°; 10·96° at 31·5°; 9·54° at 45°; 7·35° at 72°; 5·71° at 97°; 5·51° at 103°; 4·56° at 119·5°; 4·13° at 132°; 3·57° at 148°; 2·77° at 172°.

α_{5893} + 15·69° at 14°; 15·01° at 19·3°; 14·35° at 24·5°; 13·13° at 33°; 12·08° at 40·5°; 8·68° at 72°; 7·02° at 96°; 6·55° at 106°; 5·80° at 119·5°; 4·60° at 145°.

α_{5461} + 18·51° at 13°; 17·77° at 18·5°; 16·82° at 26°; 15·46° at 33·5°; 14·14° at 42·5°; 10·97° at 67°; 8·30° at 95°; 7·48° at 107°; 6·69° at 121°; 5·30° at 146°.

α_{5086} + 21·64° at 13·5°; 20·76° at 17·5°; 18·93° at 29°; 18·25° at 32°; 15·82° at 45·5°; 12·01° at 72°; 9·42° at 97°; 9·15° at 103°; 7·95° at 117°; 6·13° at 144°; 4·50° at 171°.

α_{4800} + 24·75° at 13·5°; 23·83° at 18°; 21·72° at 28°; 20·78° at 31°; 18·42° at 44°; 13·84° at 72°; 10·99° at 96°; 10·56° at 103°; 9·38° at 117°; 8·33° at 131°; 7·27° at 147°.

α_{4678} + 26·32° at 13·5°; 25·54° at 17°; 23·36° at 27°; 22·25° at 31°; 19·69° at 43·5°; 14·33° at 72°; 9·96° at 115°; 8·73° at 131°; 7·71° at 145°.

α_{4358} + 30·64° at 17°; 29·68° at 18°; 27·89° at 25°; 25·49° at 33·5°; 23·55° at 42°; 16·88° at 71°; 16·14° at 75°; 13·78° at 94°; 12·55° at 105°; 11·17° at 120°; 8·65° at 146°.

The following figures have been obtained from the smoothed curves drawn through the above values.

*Specific rotatory power of di-*d-*β-octylformal*.

		$[\alpha]_{\lambda}^{t°}$.							$\frac{[\alpha]_{4358}}{[\alpha]_{5461}}$.
$t°$.	$d_{4°}^{t°}$.	λ_{6438}.	λ_{5893}.	λ_{5461}.	λ_{5086}.	λ_{4800}.	λ_{4678}.	λ_{4358}.	
20	0·8499	+28·56°	35·14°	41·28°	48·00°	54·99°	58·61°	68·20°	1·65
40	0·8342	24·16	29·10	34·89	40·40	46·17	49·05	57·53	1·65
60	0·8158	20·20	23·96	28·93	33·58	37·72	39·75	47·56	1·65
80	0·8028	16·89	20·13	23·92	27·65	31·81	33·36	39·24	1·64
100	0·7871	14·22	17·43	20·20	23·37	27·45	28·59	33·40	1·65
120	0·7714	11·80	14·98	17·37	19·97	23·71	24·89	28·52	1·64
140	0·7557	10·19	12·71	14·82	16·94	20·43	21·44	24·48	1·65

The rotatory dispersion of the formal may be represented at 20° by the equation $[\alpha]_{\lambda}^{20°} = 10·83/(\lambda^2 - 0·033)$.

Ethyl d-β-*octyl carbonate.*

	$t°$.	18	40	74	77	129	
	$d^{t°}_{4°}$.	0·9136	0·8892	0·8586	0·8543	0·8052	
λ	6708	6402	6096	5896	5882	5790	5782	5700
$n^{20°}_{\lambda}$	1·4150	1·4159	1·4168	1·4175	1·4176	1·4180	1·4181	1·4189
λ	5461	5218	5153	5105	4358			
$n^{20°}_{\lambda}$	1·4194	1·4214	1·4208	1·4209	1·4264			

Rotatory power.

a_{5893} + 3·39° at 19°; 2·75° at 48°; 2·04° at 78°; 1·65° at 108°; 1·32° at 136°; 1·13° at 160°; 0·97° at 180°.

a_{5461} + 3·99° at 19°; 3·37° at 43°; 2·41° at 78°; 1·95° at 108°; 1·58° at 134°; 1·26° at 162°; 1·12° at 180°.

a_{4358} + 6·58° at 19°; 5·50° at 43°; 3·98° at 78°; 3·24° at 108°; 2·64° at 134°; 2·10° at 161°; 1·80° at 180°.

Values obtained from the smoothed curves.

$t°$.	20.	40.	60.	80.	100.	120.	140.	160.	180.
$d^{t°}_{4°}$.	0·9110	0·8913	0·8717	0·8521	0·8325	0·8130	0·7935	0·7740	0·7542
$[a]^{t°}_{5893}$.	+7·37°	6·56°	5·74°	4·95°	4·28°	3·69°	3·28°	2·90°	2·57°
$[a]^{t°}_{5461}$	8·74	7·75	6·75	5·83	5·05	4·34	3·78	3·31	2·97
$[a]^{t°}_{4358}$	14·37	12·59	10·90	9·49	8·29	7·25	6·31	5·48	4·78

Di-d-β-*octyl carbonate.*

$d^{t°}_{4°}$ 0·8828 at 19°; 0·8608 at 45°; 0·8349 at 79°; 0·7843 at 138°.

λ	6708	6402	6096	5896	5882	5790	5782
$n^{20°}_{\lambda}$	1·4280	1·4288	1·4298	1·4305	1·4306	1·4309	1·4309
λ	5700	5461	5218	5153	5105	4675	4358
$n^{20°}_{\lambda}$	1·4313	1·4325	1·4335	1·4341	1·4343	1·4373	1·4399

Rotatory power.

a_{5893} + 6·82° at 13·5°; 5·63° at 49·5°; 5·21° at 60·5°; 4·60° at 90°; 4·11° at 114°; 3·90° at 138°.

a_{5461} + 8·02° at 13·5°; 6·57° at 49°; 6·04° at 61·5°; 5·33° at 86°; 4·74° at 117·5°; 4·34° at 133°; 4·26° at 148°; 4·12° at 156°.

a_{4358} + 13·26° at 13·5°; 10·72° at 50°; 10·04° at 62°; 8·90° at 86·5°; 7·71° at 116·5°; 7·20° at 136°; 7·00° at 151°; 6·83° at 155°.

Values obtained from the smoothed curves.

$t°$.	20.	40.	60.	80.	100.	120.	140.
$d^{t°}_{4°}$.	0·8820	0·8653	0·8488	0·8323	0·8158	0·7992	0·7829
$[a]_{5893}$	+15·00°	13·76°	12·50°	11·50°	10·73°	10·10°	9·71°
$[a]_{5461}$	17·60	15·96	14·43	13·28	12·39	11·65	11·00
$[a]_{4358}$	29·93	26·33	23·91	22·11	20·38	19·04	18·20

Tri-l-β-*octyl orthoformate.*

$d^{t°}_{4°}$ 0·8592 at 15°; 0·8140 at 56·5°; 0·7485 at 116·5°.

$n^{15°}_{D} = 1·4376$.

Rotatory power.

a_{5893} − 8·72° at 14·5°; 7·40° at 37°; 6·18° at 67°; 5·19° at 101°; 5·02° at 112·5°; 4·80° at 130°.

a_{5461} − 10·19° at 14·5°; 8·89° at 37°; 7·35° at 69°; 6·25° at 103°; 5·98° at 112°; 5·57° at 130°.

a_{4358} − 16·94° at 14·5°; 14·47° at 37°; 12·13° at 72°; 10·33° at 103°; 9·88° at 113·5°; 9·30° at 128°.

Values obtained from the smoothed curves.

$t°$.	20.	40.	60.	80.	100.	120.
d_4^t.	0·8535	0·8319	0·8100	0·7881	0·7665	0·7448
$[\alpha]_{5893}$	−19·58°	17·50°	15·84°	14·47°	13·60°	13·22°
$[\alpha]_{5461}$	23·09	20·98	19·30	17·52	16·31	15·57
$[\alpha]_{4358}$	38·13	34·38	31·80	29·42	27·40	25·79

Di-d-β-*octyl sulphite.*

$d_4^{17°} = 0·9264$

λ	6708	6402	6096	5896	5882	5790	5782
$n_\lambda^{20°}$	1·4401	1·4412	1·4422	1·4429	1·4430	1·4435	1·4436
λ	5700	5461	5218	5153	5105	4358	
$n_\lambda^{20°}$	1·4438	1·4449	1·4462	1·4467	1·4469	1·4530	

Rotatory power.

λ	6708	5893	5461	4555 *	4481 *	4358	4144 *
$[\alpha]_\lambda^{17°}$	−14·09°	18·43°	21·98°	32·4°	35·1°	37·80°	40·5°
λ	4085 *	3998 *	3912 *	3830 *			
$[\alpha]_\lambda^{17°}$	43·2°	45·8°	48·5°	51·3°			

* Photographic measurements.

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CLXXVII.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XXIII. The Normal Aliphatic Ethers of* d-γ-*Nonanol.*

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MUCH stress has been laid, in the earlier parts of this investigation, on the fact that optically active compounds of fairly simple chemical structure may be divided into two classes as a result of a study of their rotatory dispersion. The basis of the classification depends on the form of the curve obtained when $1/\alpha$ is plotted against λ^2 (where α is the rotatory power observed for light of wave-length λ). A straight line is obtained for the simpler alcohols (Parts I, II, and IV), ethers (Parts XIV and XV), a formal, an orthoformate, a carbonate, and a sulphite (Part XXII), whilst a hyperbolic curve is obtained for most esters (Parts V, VII, VIII, and XVI). It has been pointed out that the observed dispersions of the first class can be represented by a one-term Drude equation, and therefore it was

considered that the compounds were optically and chemically homogeneous. The dispersion of these compounds was termed simple or, adopting the nomenclature given in Part XXI, normal. The members of the second class were considered to be optically and probably chemically heterogeneous in that their dispersion equations required two terms. The dispersion of this class of compounds was said to be complex, or, in the nomenclature of Part XXI, potentially anomalous. In order to account for the optical heterogeneity of these compounds, the existence of a labile or dynamic form of isomerism in these cases has been postulated.

With the object of extending the experimental data from which deductions might be drawn, a third series of optically active ethers derived from an alcohol of slightly different constitution from those previously used, namely *d*-γ-nonanol, was prepared. The labour involved in the preparation and detailed examination of this series has been fully justified by the novelty of the results obtained. Measurements of rotatory dispersion carried out with the ethers of *d*-β-octanol and of *d*-benzylmethylcarbinol showed that the relationship between $1/\alpha$ and λ^2 was apparently linear throughout the visible spectrum. The dispersion of these compounds was therefore said to be simple and the substances themselves were considered to be both chemically and optically homogeneous. This conclusion, taken in conjunction with the chemical evidence that ethers as a class are comparatively non-reactive, and the physical evidence that they are not associated in the liquid state, was considered to accord well with the hypothesis that chemical and optical homogeneity go hand in hand.

The measurements of rotatory dispersion recorded in this communication, however, do not fall into line with those previously recorded. The curves obtained by plotting $1/\alpha$ against λ^2 throughout the visible spectrum for all these ethers are apparently linear, but the numerical values of the rotatory powers of all the ethers are so small that little reliance can be placed on this fact. Fortunately, however, other evidence is available which indicates that the rotatory dispersions of the ethers now described cannot be expressed by a Drude equation with one term. The dispersion ratios, $\alpha_{4358}/\alpha_{5461}$, of these compounds in the homogeneous state have been calculated from the data given in Table III, and it has been found that, with the single exception of the methyl ether, this figure is in no case greater than 1·54, and, in general, lies between 1·40 and 1·50. If the rotatory dispersion of a substance can be represented by a one-term Drude equation, then its dispersion ratio, $\alpha_{4358}/\alpha_{5461}$, will be represented by $\frac{0{\cdot}5461^2 - \lambda_0^2}{0{\cdot}4358^2 - \lambda_0^2}$ which,

when λ_0 is smaller than the wave-lengths of the lights used to measure the dispersion ratio, has its minimum value when $\lambda_0^2 = 0$, becoming then equal to 1·57. It follows, therefore, that with the possible exception of the methyl member, the rotatory dispersions of the ethers of this series cannot be represented by a one-term Drude equation, and that we are here dealing with cases of optical heterogeneity apparently unaccompanied by chemical heterogeneity. Further discussion of these results must be postponed until more evidence is available. It may be urged, of course, that the fact that the numerical values of the observed rotatory powers of these compounds are so small renders the values of the dispersion ratios uncertain, but it must be pointed out that these ratios are consistent amongst themselves and are all, with the exception of those for the methyl ether, lower than 1·57.

Finally, it may be noted that, if the values for $[\alpha]_{5461}^{20°}$ for this series of ethers be plotted against the number of carbon atoms in the growing alkyl group attached to the ethereal oxygen atom, a smooth curve is obtained, showing, however, a characteristic depression at the *n*-propyl member, and a similar, but much smaller, depression at the *n*-octyl member, where the group contains five more carbon atoms (compare Part XIII).

Experimental.

d-γ-*Nonanol*.—The optically active alcohol was prepared by the method described in Part I. γ-Nonyl hydrogen phthalate (1370 grams) was combined with strychnine (1540 grams) and the resulting salt fractionally crystallised from ethyl alcohol. The pure *l*B,*d*A salt (yield 500 grams) gave 105 grams of pure *d*-γ-nonanol, b. p. 94°/15 mm., $\alpha_D^{20°} + 6·75°$ ($l = 1$).

Action of Potassium on d-γ-*Nonanol*.—Seven grams of a partly resolved sample of *d*-γ-nonanol ($\alpha_D + 4·97°$) were added to powdered potassium (2 grams), covered with dry benzene. After complete dissolution of the metal the potassium alkyloxide was decomposed with water. The regenerated alcohol had α_D 4·95°, showing that no racemisation had taken place.

General Method of Preparation of the Active Ethers.—The procedure is described in Parts XIV and XV. Potassium (3 grams) having reacted with *d*-γ-nonanol (15 grams) in dry ether, the solution was boiled with a slight excess of the requisite alkyl halide, the product freed from uncombined *d*-γ-nonanol by heating with an excess of phthalic anhydride, and the ether redistilled until its rotatory power and refractive index were constant (yield 4·5—6 grams; about 7 grams of optically pure *d*-γ-nonanol were recovered).

Table I.

Ethers of d-γ-*nonanol.*

Densities ($d^{t°}_{4°}$), refractive indices ($n^{20°}_{D}$), and boiling points.

Methyl Ether. B. p. 74°/15 mm. $n^{20°}_{D}$ 1·4154.
$d^{t°}_{4°}$ 0·7926 at 23°; 0·7743 at 45°; 0·7571 at 67°; 0·7384 at 88°; 0·7260 at 103°; 0·7027 at 130°.

Ethyl Ether. B. p. 88°/21 mm. $n^{20°}_{D}$ 1·4164.
$d^{t°}_{4°}$ 0·7901 at 22°; 0·7769 at 40°; 0·7606 at 61°; 0·7453 at 80°; 0·7256 at 105°; 0·7049 at 130°.

n-*Propyl Ether.* B. p. 103°/23 mm. $n^{20°}_{D}$ 1·4193.
$d^{t°}_{4°}$ 0·7961 at 21°; 0·7811 at 41°; 0·7655 at 60°; 0·7506 at 79°; 0·7319 at 101°; 0·7008 at 137°.

n-*Butyl Ether.* B. p. 114°/19 mm. $n^{20°}_{D}$ 1·4226.
$d^{t°}_{4°}$ 0·7978 at 21°; 0·7835 at 41°; 0·7682 at 61°; 0·7518 at 82°; 0·7302 at 109°; 0·7134 at 129°.

n-*Amyl Ether.* B. p. 123°/15 mm. $n^{20°}_{D}$ 1·4257.
$d^{t°}_{4°}$ 0·8017 at 21°; 0·7877 at 40°; 0·7725 at 61°; 0·7580 at 80°; 0·7390 at 106°; 0·7200 at 130°.

n-*Hexyl Ether.* B. p. 138°/17 mm. $n^{20°}_{D}$ 1·4283.
$d^{t°}_{4°}$ 0·8048 at 22°; 0·7917 at 40°; 0·7765 at 61°; 0·7599 at 80°; 0·7479 at 99°; 0·7176 at 137°.

n-*Heptyl Ether.* B. p. 155°/18 mm. $n^{20°}_{D}$ 1·4310.
$d^{t°}_{4°}$ 0·8101 at 17°; 0·8069 at 20°; 0·7919 at 42°; 0·7695 at 74°; 0·7474 at 104°; 0·7241 at 134°.

n-*Octyl Ether.* B. p. 166°/17 mm. $n^{20°}_{D}$ 1·4335.
$d^{t°}_{4°}$ 0·8085 at 24°; 0·7967 at 41°; 0·7794 at 67°; 0·7667 at 85°; 0·7486 at 108°; 0·7287 at 134°.

n-*Nonyl Ether.* B. p. 176°/17 mm. $n^{20°}_{D}$ 1·4356.
$d^{t°}_{4°}$ 0·8082 at 24°; 0·7962 at 42°; 0·7816 at 65°; 0·7694 at 82°; 0·7522 at 106°; 0·7306 at 133°.

Table II.

Ethers of d-γ-*nonanol.*

Observed rotations in a 50 mm. jacketed tube at different temperatures.

Methyl Ether.
λ = 6708 −0·35° at 20°; − 0·35° at 47°; − 0·36° at 75°; − 0·39° at 89°; − 0·40° at 109°.
λ = 5893 − 0·48° at 20°; − 0·51° at 47°; − 0·55° at 75°; − 0·51° at 89°; − 0·53° at 109°.
λ = 5780 − 0·48° at 20°; − 0·56° at 89°; − 0·55° at 109°.
λ = 5461 − 0·56° at 20°; − 0·56° at 47°; − 0·58° at 75°; − 0·61° at 89°; − 0·63° at 109°.
λ = 4358 − 1·19° at 20°; − 1·20° at 47°; − 1·21° at 75°; − 1·27° at 89°; − 1·25° at 100°; − 1·28° at 109°.

Ethyl Ether.

λ = 6708 + 0·82° at 21°; 0·68° at 63°; 0·56° at 87°; 0·42° at 107°; 0·35° at 137°.
λ = 5893 1·01° at 21°; 0·77° at 63°; 0·63° at 87°; 0·52° at 107°; 0·42° at 135°.
λ = 5780 1·04° at 21°; 0·79° at 63°.
λ = 5461 1·15° at 21°; 0·84° at 64°; 0·68° at 87°; 0·58° at 107°; 0·45° at 135°.
λ = 4358 1·73° at 21°; 1·20° at 63°; 1·00° at 86°; 0·84° at 107°; 0·6° at 136°.

n-*Propyl Ether.*

λ = 6708 + 0·77° at 17°; 0·62° at 42°; 0·56° at 63°; 0·50° at 86°; 0·45° at 104°.
λ = 5893 0·94° at 17°; 0·76° at 44°; 0·67° at 63°; 0·60° at 103°; 0·52° at 129°.
λ = 5780 0·98° at 17°; 0·82° at 44°; 0·70° at 63°.
λ = 5461 1·08° at 17°; 0·90° at 44°; 0·78° at 63°; 0·64° at 85°; 0·65° at 103°; 0·60° at 129°.
λ = 4358 1·62° at 17°; 1·30° at 44°; 1·06° at 63°; 0·87° at 86°; 0·80° at 103°; 0·76° at 129°.

n-*Butyl Ether.*

λ = 6708 + 1·11° at 18°; 1·01° at 48°; 0·96° at 57°; 0·90° at 67°; 0·84° at 92°; 0·75° at 118°; 0·70° at 134°.
λ = 5893 1·35° at 18°; 1·19° at 49°; 1·08° at 67°; 0·92° at 112°; 0·84° at 135°.
λ = 5780 1·40° at 18°; 1·22° at 47°; 1·16° at 58°; 1·11° at 67°; 1·04° at 92°; 0·96° at 118°.
λ = 5461 1·54° at 18°; 1·34° at 48°; 1·25° at 67°; 1·12° at 95°; 1·07° at 118°; 0·97° at 140°.
λ = 4358 2·33° at 18°; 2·12° at 48°; 1·99° at 56°; 1·86° at 67°; 1·55° at 119°; 1·45° at 140°.

n-*Amyl Ether.*

λ = 6708 + 1·10° at 18°; 0·92° at 58°; 0·82° at 86°; 0·79° at 95°; 0·76° at 106°; 0·70° at 139°.
λ = 5893 1·33° at 18°; 1·17° at 58°; 1·00° at 86°; 1·00° at 95°; 0·95° at 111°; 0·89° at 139°.
λ = 5780 1·38° at 18°; 1·21° at 58°; 1·15° at 86°; 1·04° at 111°; 0·98° at 139.°
λ = 5461 1·52° at 18°; 1·34° at 58°; 1·17° at 96°; 1·15° at 111°; 1·15° at 139°.
λ = 4358 2·33° at 18°; 1·97° at 58°; 1·68° at 86°; 1·73° at 96°; 1·65° at 111°; 1·55° at 139°.

n-*Hexyl Ether.*

λ = 6708 + 1·00° at 20°; 0·89° at 65°; 0·82° at 89°; 0·81° at 104°; 0·73° at 130°.
λ = 5893 1·28° at 20°; 1·07° at 65°; 1·00° at 90°; 0·95° at 104°; 0·93° at 130°.
λ = 5780 1·34° at 20°; 1·14° at 65°; 0·97° at 130°.
λ = 5461 1·48° at 20°; 1·30° at 65°; 1·15° at 92°; 105° at 109°; 1·08° at 130°.
λ = 4358 2·18° at 20°; 1·90° at 65°; 1·70° at 89°; 1·53° at 106°; 1·50° at 130°.

n-*Heptyl Ether.*

λ = 6708 + 0·97° at 20°; 0·86° at 60°; 0·81° at 86°; 0·73° at 102°; 0·68° at 135°.
λ = 5893 1·20° at 20°; 1·10° at 60°; 1·01° at 86°; 0·93° at 101°; 0·82° at 135°.
λ = 5780 1·26° at 20°; 1·14° at 60°; 1·07° at 86°; 0·96° at 101°; 0·86° at 135°.
λ = 5461 1·45° at 20°; 1·26° at 60°; 1·20° at 86°; 1·05° at 101°; 0·96° at 130°.
λ = 4358 2·16° at 20°; 1·90° at 60°; 1·66° at 86°; 1·46° at 101°; 1·42° at 106°; 1·34° at 130°; 1·20° at 138°.

n-*Octyl Ether.*

$\lambda = 6708$ + 0·95° at 18°; 0·84° at 51°; 0·76° at 80°; 0·71° at 95°; 0·58° at 130°.
$\lambda = 5893$ 1·19° at 19°; 1·06° at 51°; 0·90° at 80°; 0·86° at 95°; 0·70° at 130°.
$\lambda = 5780$ 1·23° at 19°; 1·10° at 51°; 0·95° at 80°; 0·90° at 95°; 0·74° at 130°.
$\lambda = 5461$ 1·33° at 19°; 1·20° at 51°; 1·05° at 80°; 0·95° at 95°; 0·78° at 130°.
$\lambda = 4358$ 1·91° at 19°; 1·66° at 51°; 1·50° at 80°; 1·40° at 95°; 1·15° at 130°.

n-*Nonyl Ether.*

$\lambda = 6708$ + 0·95° at 17°; 0·84° at 59°; 0·78° at 90°; 0·70° at 114°; 0·64° at 137°.
$\lambda = 5893$ 1·18° at 17°; 1·04° at 59°; 0·86° at 114°; 0·82° at 137°.
$\lambda = 5780$ 1·21° at 17°; 1·10° at 57°; 1·00° at 90°; 0·88° at 114°; 0·82° at 137°.
$\lambda = 5461$ 1·34° at 17°; 1·18° at 57°; 1·07° at 90°; 0·95° at 114°; 0·86° at 137°.
$\lambda = 4358$ 1·93° at 17°; 1·66° at 57°; 1·54° at 90°; 1·22° at 114°; 1·20° at 136°.

TABLE III.

Specific rotatory powers of the ethers of d-γ-*nonanol in* (a) *carbon disulphide and* (b) *ethyl alcohol at room temperature* ($c = 5$).

Ether.		$[\alpha]_\lambda$.				
		$\lambda = 6708$.	5893.	5780.	5461.	4358.
Methyl	(a)	+ 8·2°	+ 10·7°	+ 11·4°	+ 14·1°	+ 23·3°
	(b)	1·0	1·1	0·9	1·1	1·5
Ethyl	(a)	13·6	17·7	19·7	21·8	37·1
	(b)	5·1	6·5	7·7	7·9	11·9
n-Propyl	(a)	12·0	16·5	18·4	20·9	35·1
	(b)	3·1	4·2	4·0	4·9	7·6
n-Butyl	(a)	14·3	18·4	21·4	23·6	38·6
	(b)	5·1	6·4	6·2	7·4	10·4
n-Amyl	(a)	13·8	17·0	17·8	20·6	36·0
	(b)	4·3	5·3	5·4	6·0	8·6
n-Hexyl	(a)	14·2	17·4	18·9	20·7	35·2
	(b)	4·2	5·4	5·0	5·9	8·7
n-Heptyl	(a)	12·7	14·4	16·9	19·7	32·2
	(b)	4·0	5·1	4·8	5·5	8·2
n-Octyl	(a)	11·0	13·9	16·1	17·3	29·5
	(b)	3·5	4·6	4·7	5·3	7·8
n-Nonyl	(a)	11·7	14·9	16·7	18·2	30·6
	(b)	4·0	4·7	5·0	5·7	7·9

The materials used in this investigation were, in part, purchased from a grant from the Government Grant Committee of the Royal Society, to whom the authors express their thanks.

BATTERSEA POLYTECHNIC, S.W. 11. [*Received, February 1st*, 1924.]

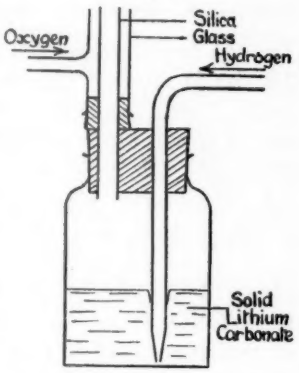
NOTES.

An Intense Lithium Flame for Polarimetric Use. By HAROLD HUNTER.

THE red lithium line at $\lambda = 6708$ Å. would be of very great use in measurements of rotatory dispersion, but the attempts hitherto made to produce a suitable lithium flame (Lowry, *Phil. Trans.*, 1912, **212**, 270; Manley, *Phil. Mag.*, 1923, [vi], **45**, 336) have been unsatisfactory owing to the unsteadiness and evanescence of the flame or its lack of intensity. With the following device, an intense, steady lithium flame can be maintained for a length of time limited only by the supply of gas to the burner.

Hydrogen from a cylinder is led by means of a jet through a bottle containing a layer of dry lithium carbonate, at least 3 cm. thick (in order that the powder may not be blown permanently away from the jet), and thence through a silica tube which acts as burner. This tube (see Fig.) is jacketed with a glass tube by means of which oxygen is supplied to the flame. The burner tube must be of silica. No other material, except perhaps platinum, will stand the high temperature without imparting an undesirable colour to the flame. The burner corrodes in time, possibly by the formation of lithium silicate, but the damaged portion may be ground away when necessary. "Pure" lithium carbonate contains sufficient sodium to give an intense colour to the flame. With a direct-vision spectroscopic eyepiece, it is then easy to read both the lithium and the sodium lines with one burner. The orange lithium line is too faint to be read.—BATTERSEA POLYTECHNIC, S.W. 11. [*Received, April 23rd*, 1924.]

FIG. 1.



Sulphonation of m-*Dinitrobenzene.* By ROLAND HALL GRIFFITH.

3 : 5-DINITROBENZENESULPHONIC ACID (Limpricht, *Ber.*, 1876, **9**, 554; Sachse, *Annalen*, 1877, **188**, 143; Jackson and Earle, *J. Amer. Chem. Soc.*, 1903, **29**, 218) can be prepared by the direct sulphonation of *m*-dinitrobenzene thus: a mixture of 50 grams of *m*-dinitrobenzene with 150 c.c. of 18 per cent. oleum and 4—5 grams of mercury is heated at 150—160° for 8 or 9 hours, cooled,

the product poured on to ice, and neutralised with milk of lime. The deep purple colour of the filtrate from the calcium sulphate changes to orange as the liquid is evaporated. The potassium salt is obtained by adding the calculated quantity of potassium carbonate and evaporating the solution until crystallisation begins (yield 38 per cent.) (Found: $H_2O = 8{\cdot}4$; $K = 13{\cdot}3$. Calc., $H_2O = 8{\cdot}6$; $K = 13{\cdot}6$ per cent.).

Barium hydroxide cannot be so satisfactorily used as milk of lime, as the product is sensitive to alkali and appears to change readily into a nitrohydroxy-sulphonic acid. Excess of potassium carbonate must be avoided for the same reason.—Dyson Perrins Laboratory, Oxford. [*Received, February 27th*, 1924.]

Tellurium Monoxide. By J. J. Doolan and J. R. Partington. Divers and Shimosé (*J. pr. Chem.*, 1881, [ii], **24**, 218; *Ber.*, 1883, **16**, 1004) studied the decomposition by heat of tellurium sulphoxide, $TeSO_3$, analogous to S_2O_3 and $SeSO_3$, produced by the interaction of sulphuric anhydride and tellurium. Weber (*J. pr. Chem.*, 1882, [ii], **25**, 218) stated that the sulphoxide, when heated on the water-bath, gives off sulphur dioxide, leaving tellurium and tellurous acid, and also that the compound decomposes if kept, even in sealed tubes, at the ordinary temperature, but rapidly above 35°. Divers and Shimosé, on the other hand, maintained that $TeSO_3$ is stable at the ordinary temperature in the absence of moisture, that it may be heated at 180° in a vacuum without decomposition, but that above 180° it yields tellurium monoxide: $STeO_3 = SO_2 + TeO$.

No compound SO has been prepared, and the corresponding selenium compound, SeO, which Berzelius and later Chabrié (*Bull. Soc. chim.*, 1889, [iii], **2**, 788; *Ann. Chim. Phys.*, 1890, [vi], **20**, 273) describe, respectively, as a gas and as a solid, has, apparently, no real existence (Lenher, *J. Amer. Chem. Soc.*, 1898, **20**, 555; Rathke, *Ber.*, 1903, **36**, 600).

The tellurium sulphoxide was prepared exactly according to the method described by Divers and Shimosé. The mode of decomposition by heat was next studied. A sealed tube of the sulphoxide was attached to a Sprengel pump, the end broken, and evacuation carried on through a tube filled with borax until adherent sulphur trioxide had disappeared. The sulphoxide was maintained in a vacuum at 35—40° for 2½ hours without change. The temperature was gradually raised to 65°. The red, cellular mass shrank very slightly and in places began to turn brown. The temperature was gradually increased to 90°, at which point

the steady change to brown did not appear materially to increase in speed, but it was noticed that a slight evolution of gas occurred. The brown colour persisted while the temperature rose to 180°. The colour now commenced to darken to black. The temperature was maintained for a considerable time at 255° without further change. The mass, which was now quite black, was removed, powdered, and purified by washing with dilute sodium carbonate to remove sulphur compounds and any possible tellurous acid, followed by hot water and alcohol, and was finally dried. The grey powder obtained resembled in appearance very finely powdered tellurium, but its density was considerably less than that of tellurium.

The substance was analysed by conversion into dioxide by Scott's method ("Standard Methods of Chemical Analysis," 1922, p. 427), which gave more consistent results than that described by Divers and Shimosé [Found : Te = 87·84. Calc. (TeO) = 88·85 per cent.].

Divers and Shimosé's statement that no swelling occurred with heated sulphuric anhydride was verified. The black powder was found to decolorise potassium permanganate solution practically instantaneously even in the cold. The existence of the oxide TeO would appear, therefore, to be confirmed by these experiments.

The authors wish to thank the American National Council for Research on Selenium and Tellurium for generously placing at their disposal a considerable quantity of tellurium for these and other experiments.—East London College, University of London. [*Received, February 20th,* 1924.]

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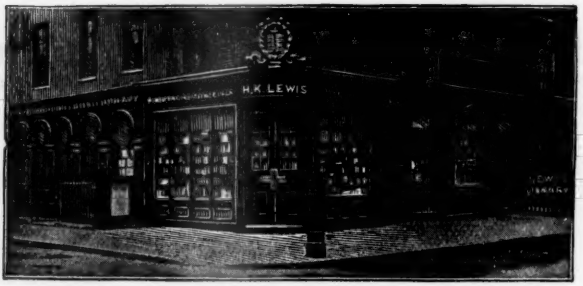

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ERRATA.

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Page		Line	
1912		16	*for* " Vignerie " *read* " Viguerie."
,,	(last col.)	17—25	*for* " 118·05, 90·92, non dosée, 27·02, (S. Humages) non dosée, non dosée, 65·96, non dosée, 60·74 " *read* " 132·5, 107·0, 55·5, 28·0, (S. Etuves) 8·6, non dosée, 76·7, 8·2, 82·5."
1914	(last col.)	16	*for* " 141·50 " *read* " 161·4."
1917		24*	*for* " 6·077 10·020 " *read* " 6,077 10,020."
,,		12*	*for* " 65,486 " *read* " 69,800."
1918		4	
1923	Table IV, last col.		*for* " Ar " *read* " Kr."
,,		20*	*for* " 1·8 " *read* " 1·2."
,,		19*	*for* " No. 8 " *read* " No. 2."
,,		1*	*for* " 24·814 " *read* " 24,814."
1926		18*	*for* " 1·000 " *read* " 1·004."
,,		17*	*for* " 1 " *read* " 1·004."
1930		9*	*for* " Shutt " *read* " Strutt."
1931		18	*for* " $1{\cdot}5^{-12}$ " *read* " $1{\cdot}5 \times 10^{-12}$."
,,		19	*for* " $1{\cdot}2^{-5}$ " *read* " $1{\cdot}2 \times 10^{-5}$."
1932		3*	*for* " Leche " *read* " Zeche."
1936	Table XI, 2nd col.		*for* " 1·18 " *read* " 1·195."
,,	,, 3rd col.		*for* " 0·82, 0·97, 0·85, 1·72, 1·38 " *read* " 0·81, 0·96, 0·84, 1·70, 1·36."
1938		15	*for* " Ysère " *read* " Isère."
1939		19	*for* " 0·25 " *read* " 0·26."
1940		4	*for* " notablement plus élevé " *read* " du même ordre."
,,		5	*for* " Anzin, 4380 mètres cubes " *read* " Vaux-en-Bugey, 20,747 mètres cubes."
,,		14	*add* " Les recherches relatives à l'hélium des gaz naturels du Canada et des Etats-Unis ont fait l'objet d'importantes publications d'ensemble dues au Professeur MacLennan et associés (Department of Mines, Bull. 31, Ottawa, 1920) et à G. S. Rogers (Department of the Interior, Professional Paper No. 121, Washington, 1921)."
1941		5	*for* " Ponzzoles " *read* " Pouzzoles."
,,		11*	*for* " toute relation de l'azote " *read* " inertie toute relative de l'azote."
3155		3	*for* " 1·5/4·22 " *read* " 1·22/1·5."

VOL. 125 (1924).

426		4	*for* " $1{\cdot}3 \times 10^{-12}$ " *read* " $1{\cdot}07 \times 10^{-12}$."
,,		5	*for* $1{\cdot}0 \times 10^{-12}$ " *read* " $1{\cdot}03 \times 10^{-12}$."
1049		13*	*for* " *m*-hydroxybenzoic " *read* " *m*-nitrobenzoic."

* From bottom.

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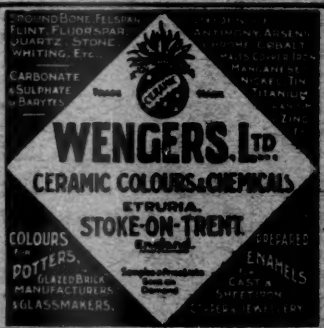
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